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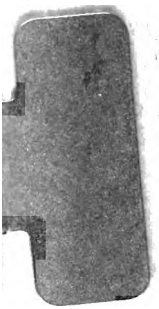

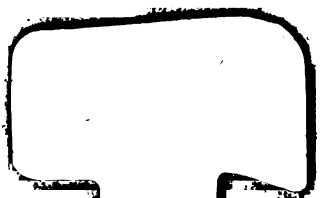

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THE

CHEMICAL GAZETTE,

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JOURNAL OF PRACTICAL CHEMISTRY,

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS AND MANUFACTURES.

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WILLIAM FRANCIS, PH.D., F.L.S., F.R.A.S., F.C.S.

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THE

CHEMICAL GAZETTE.

No. CCCXLI.—January 1, 1857.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Redetermination of the Atomic Weight of Lithium. *By* J. W. MALLET, Ph.D., Professor of Chemistry, Univ. of Alabama.

LITHIUM is one of the elements whose atomic weight has been several times made the subject of investigation by different chemists, and yet on examining the results of their labours we find that but one or two experiments free from serious objection are recorded, from which the received equivalent number of the metal has been calculated; and even in these experiments the method pursued has not, I believe, been such as to ensure the closest approximation to the truth. Yet the formulæ of the salts of lithia, and of minerals containing this alkali, would be seriously affected by any considerable error as regards the equivalent number assumed, since this is one of the very lowest to be found in the whole list of elements, the lowest among the metals with the single exception of glucinum. The fact that lithium does possess so small an atomic weight, a fact which is said to have led to the discovery of the metal by Arfwedson, is in itself very remarkable when we remember the much higher numbers by which the other alkaline metals, potassium and sodium, are represented; and it gives additional interest to accurate experiments made for the purpose of fixing the number with precision.

The following historical notice of what has been already done in this direction I have taken from a valuble little work by A. C. Oudemans, Jun., published at Leyden in 1853*, which reviews the determination of the equivalents of twenty-two of the elements, chiefly those of the alkaline and earthy metals. The original memoirs I have for the most part been unable to consult; but the work of M. Oudemans supplies all necessary details of the experiments, and contains also judicious critical remarks upon the trustworthiness of the results.

In 1817 Arfwedson† discovered lithium, and in the course of his examination of the new element he obtained the following results from which to calculate its atomic weight:—

1. 5·732 grms. of LiO, SO^3, prepared by dissolving carbonate of lithia in sulphuric acid, gave 11·454 grms. of BaO, SO^3.

* Historisch-Kritisch Overzigt van de bepaling der Æquivalent-gewigten van twee en twintig metalen door A. C. Oudemans, Jr. Leiden, 1853.

† Afh. i Kemi, Fysik och Mineralogie, vi. Schweig. Journ. xxii. 93–100. Ann. de Chim. et de Phys. [2], x. 82. Pogg. Ann., viii. 189.

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2. 0·597 grm. of LiO, SO^3 appeared to consist of 0·406 grm. of SO^3 and 0·191 grm. of LiO.

3. 4·204 grms. of chloride of lithium gave 13·224 grms. of chloride of silver.

Soon after, Vauquelin* analysed anhydrous sulphate of lithia, and found 0·430 grm. of LiO, SO^3 to yield 0·875 grm. of BaO, SO^3.

C. G. Gmelin† found a little later that 0·481 grm. of LiO, SO^3, precipitated by acetate of baryta, gave 0·953 grm. of BaO, SO^3; and that the acetate of lithia produced in this experiment left on ignition 0·316 grm. of carbonate.

Stromeyer‡ also analysed sulphate of lithia, and stated its composition as—

Lithia	30·819
Sulphuric acid	69·189

In 1828 Kralovanszky§ published some experiments on the equivalent of lithium, in which experiments, as in those of preceding chemists, the precipitation of a solution of sulphate of lithia by acetate of baryta was the method employed. In one analysis, 2 grms. of neutral, strongly ignited LiO, SO^3 gave 3·985 grms. of BaO, SO^3; and a second analysis yielded a result from which a slightly higher atomic weight was deducible.

Hermann‖ was the next chemist who occupied himself with the equivalent of lithium. He prepared carbonate of lithia by precipitating a strong solution of chloride of lithium with carbonate of ammonia or of soda, washing and igniting the precipitate. A weighed quantity of this carbonate was then brought in contact with muriatic acid in a gas cylinder filled with mercury, and the carbonic acid evolved was measured. It was found in one experiment =60·98, and in another=61·00 per cent. of the carbonate of lithia. Hermann also dissolved this carbonate in sulphuric acid, evaporated to crystallization, and dried the crystals of sulphate of lithia over a spirit-lamp. 100 parts of the dry salt gave an amount of sulphate of baryta corresponding to 74 parts of sulphuric acid.

In 1831 Berzelius¶ repeated the experiments of Hermann, and with the following results:—4·4545 grms. of fused carbonate of lithia dissolved in sulphuric acid gave 6·653 grms of sulphate of lithia; and 1·874 grm. of this anhydrous sulphate gave 3·9985 grms. of sulphate of baryta.

In 1839 Hagen** re-examined with accuracy some of the minerals containing lithia, and discovered that this alkali occurred in them, not pure, as it had been previously supposed, but accompanied by soda; and as in the preparation of lithia-salts for analysis, most of the earlier chemists had taken no steps for the separation of the soda, it became obvious that most of the determinations which had been

* Ann. de Chim. et de Phys. [2], vii. 287. † Gilbert's Ann., lix. 283.
‡ Stromeyer, Untersuchungen, i. 435. Schweig. Journ., xxxiii. 373.
§ Schweig. Journ., liv. 234. Berz. Jahresb., ix. 93.
‖ Pogg. Ann., xv. 480. Berz. Jahresb., x. 96.
¶ Pogg. Ann., xvii. 379. Berz. Jahresb., x. 96.
** Pogg. Ann., xlviii. 361.

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made of the equivalent of lithium were necessarily quite erroneous; and that the results of Berzelius and Hermann alone deserved any confidence, the salts analysed by them having been prepared from precipitated carbonate of lithia *.

Hagen himself found that 1·002 grm. of pure sulphate of lithia in crystals left, on being strongly heated, 0·852 grm. of the anhydrous sulphate; and on being redissolved and precipitated with a salt of baryta, gave 1·8195 grm. of sulphate of baryta.

The above are the results of the experiments which have been made up to the present time. I have not given along with each the equivalent number deduced by the analyst himself, but have preferred to make the calculation in each case, using the most recently determined equivalents for the other substances involved in the several processes †, and I here present the results in tabular form:—

Authority.	Salt analysed.	Atomic weight of lithium.
Arfwedson, 1st exp.	Sulphate	129·30
„ 2nd exp.	Sulphate	135·22
„ 3rd exp.	Chloride	126·71
Vauquelin	Sulphate	116·17
Gmelin, 1st exp.	Sulphate	135·54
„ 2nd exp.	Sulphate conv. into carbonate	108·22
Stromeyer	Sulphate	122·74
Kralovanszky	Sulphate	131·40
Hermann, 1st exp.	Carbonate	75·97
„ 2nd exp.	Sulphate	75·82
„ 3rd exp.	Sulphate	75·67
Berzelius, 1st exp.	Carbonate conv. into sulphate	80·89
„ 2nd exp.	Sulphate	83·01
Hagen	Sulphate	82·41

Of these sufficiently discrepant numbers, those of Arfwedson, Vauquelin, Gmelin, Stromeyer, and Kralovanszky are at once to be rejected, for the reason already mentioned, that the substance analysed by each of these chemists was not in reality a pure salt of lithia, but a mixture of salts of lithia and soda. The determination by Hermann of the amount of carbonic acid in the carbonate was not conducted in a manner likely to yield the most accurate results;

* It is true that Arfwedson prepared his sulphate of lithia by dissolving the carbonate in sulphuric acid; but this carbonate seems to have been obtained by precipitating the sulphate of lithia (containing soda) with acetate of baryta, filtering, evaporating the filtrate, and igniting—a process which of course would not remove the soda.

† The equivalents used are—

Oxygen	100·00	
Chlorine	443·28	(Marignac.)
Sulphur	200·00	
Carbon	75·00	
Silver	1349·66	(Marignac.)
Barium	857·32	(Marignac.)

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and probably the same objection may be made against Berzelius's first experiment, which was made with the same salt.

We find then but three numbers apparently deserving of much confidence, namely those deduced from the analysis of anhydrous sulphate of lithia by Hermann, Berzelius and Hagen—one experiment by each of these chemists. Hermann's result differs very considerably from the other two, and, as is observed by M. Oudemans, should have less importance attached to it, since the original weighings are not recorded, but merely the per-centage of sulphuric acid deduced therefrom by the analyst. Berzelius's result has been generally taken of late years as the true one, and with it that of Hagen agrees pretty well.

We have thus the atomic weight of lithium as the result of but two experiments, agreeing it is true fairly with each other, but both made by the same process—the precipitation of sulphate of lithia by a salt of baryta, washing, igniting, and weighing the BaO, SO^3 produced. And as it is well known that sulphate of baryta is washed with extreme difficulty, an excess of the barytic salt used for precipitation obstinately adhering to the precipitate even after a very large quantity of hot water has been filtered through it—this fact rendering the exact determination of the sulphuric acid difficult; and as the quantity of sulphate of lithia submitted to analysis in each of these experiments was but small, and therefore the effect of any trifling error in the estimation of the sulphuric acid would be more seriously felt, it seemed that the equivalent of the metal might be redetermined with advantage, using a larger amount of a carefully prepared salt, better adapted to the purpose than the sulphate, and requiring the process of analysis to be varied. The salt chosen was the chloride of lithium, and I shall describe first the mode of its preparation, and then the experiments which have been made upon its composition.

Crystallized spodumene from the granite of Goshen (Mass.), where the mineral occurs with blue tourmaline, beryl, and rose-mica, was finely pulverized, and 1 part mixed with 3 or 4 of unslaked lime and about three-fourths of sal-ammoniac. The mixture was heated in large crucibles to the highest temperature of a good wind-furnace. This is the process proposed by Prof. J. L. Smith* for the analysis of silicates, except that he uses carbonate of lime instead of the caustic earth. The nearly fused mass was pulverized, mixed with water, and treated with sulphuric acid in excess. The solution was filtered off from the sulphate of lime and other insoluble matter, and the latter washed with plenty of water upon a cloth filter. The still milky liquid was boiled down to a moderate bulk, and precipitated with chloride of barium; the sulphate of baryta thrown down was washed by decantation, and the solution was filtered through paper. The filtrate was now a solution of chloride of lithium, free from sulphuric acid, but containing the chlorides of several other metals in admixture. It was carefully evaporated to dryness to get rid of any silicic acid, redissolved, precipitated with

* Chem. Gaz., vol. xi. pp. 252, 333.

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ammonia, sulphuret of ammonium and carbonate of ammonia, filtered, evaporated to dryness, and the residue heated until all ammoniacal salts were expelled. The residue was then redissolved, the solution boiled with a little pure milk of lime, and filtered from magnesia. The lime in the filtrate was removed by oxalate of ammonia, and the solution was evaporated to dryness, and heated to expel salts of ammonia. The residue, now containing only the alkaline chlorides, was moistened with a little water, and again dried at a gentle heat, not over 100° C. The dry mass was introduced into a glass-stoppered bottle, and a mixture of equal volumes of æther and absolute alcohol was poured upon it, solution of the chloride of lithium being aided by shaking the bottle from time to time. After a few hours the clear liquid was decanted, and the alcohol and æther were distilled off. The dry residue left by the distillation of this first alcoholic solution was again treated with æther and alcohol, the liquid again decanted and distilled, and finally the same process of purification was repeated a third time, nothing being now left undissolved by the æther-alcohol. The pure chloride of lithium was fused in a covered platinum crucible, poured out upon a sheet of platinum, and the fused mass broken up while warm, and quickly enclosed in a bottle with a well-ground stopper.

This anhydrous chloride of lithium was beautifully clear and colourless, and a portion of it taken for careful qualitative examination appeared to be perfectly pure; it was, at least, completely free from any traces of the earths or heavy metallic oxides, and might be fairly supposed to have been also freed from all chloride of sodium or potassium by the repeated treatment with æther and absolute alcohol.

On fusion in an uncovered vessel for some time, the salt loses a little chlorine, and takes up oxygen, so that when redissolved in water it reacts alkaline to test-paper; but it was found that this change could be completely avoided by mixing a little pure sal-ammoniac with the chloride of lithium before evaporation to dryness, and fusing the dry mass in a covered crucible. The heat applied must not be too great until the sal-ammoniac has been driven off, as in a first experiment, in which the quantity of NH^4Cl was considerable and the heat rapidly applied, the greater part of the chloride of lithium was volatilized and lost, although the platinum crucible was covered and was not raised to more than a low red heat.

Having got then pure fused chloride of lithium, it remained to determine its composition, or the per-centage of chlorine which it contains. The salt is a deliquescent one, and it seemed doubtful at first whether the absorption of moisture could be prevented during weighing, but it was found that in a platinum crucible provided with a tightly-fitted cover, the portion taken for analysis, consisting of but three or four fragments of the fused cake, could be weighed with ease and certainty, the weight remaining constant for more than five minutes in the hot dry atmosphere of a summer day. The balance used was an excellent one of Berlin make, permitting of accurate weighing to the one-tenth of a milligramme. Both it and the weights

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used were subjected to a careful examination as to adjustment beforehand.

Three or four pieces of the fused chloride of lithium were placed in the platinum crucible used for weighing, the cover was put on, and then the vessel was heated for some time to a temperature not much below the fusing-point of the salt. The crucible was cooled over oil of vitriol, weighed, reheated, again cooled, and a second time placed upon the balance, so as to observe perfect correspondence between the two weighings. The fragments of chloride of lithium were then placed in a beaker of convenient size, and dissolved in water, while the crucible was once more heated, cooled, and weighed; its weight now being subtracted from the former weighing, gave the amount of LiCl used. The solution of LiCl was precipitated by a slight excess of nitrate of silver, the solution gently heated to condense the precipitate, and the latter washed with very dilute nitric acid and then with pure water, first by decantation, and afterwards upon a filter through which all the decanted liquid had been passed. When perfectly washed, the filter with chloride of silver was carefully dried, and the chloride of silver transferred as a single lump to a counterpoised porcelain crucible, upon the lid of which the filter was burned, the ashes being moistened with nitric and then with hydrochloric acid. The lid was placed upon the crucible, the latter was heated until the chloride of silver began to fuse, and was then cooled over oil of vitriol and weighed.

Two experiments made by the above method gave the following results:—

1. 7·1885 grms. of LiCl gave 24·3086 grms. of AgCl.
2. 8·5947 grms. of LiCl gave 29·0621 grms. of AgCl.

Now—

24·3086 : 7·1885 :: 1792·94 (equiv. of AgCl) : x

$x = 530{\cdot}21$ (equiv. of LiCl).

530·21 − 443·28 (equiv. of Cl) = 86·93 = equiv. of Li and

29·0621 : 8·5947 :: 1792·94 : x

$x = 530{\cdot}24$

530·24 − 443·28 = 86·96 = equiv. of Li,

the two numbers thus obtained for lithium agreeing with remarkable closeness.

The difference between these numbers and those of Berzelius and Hagen is however considerable; and as it seemed possible that a little chloride of sodium, still retained in spite of the purification by æther-alcohol, might be the cause of this difference, I resolved to precipitate a solution of this supposed pure chloride of lithium with carbonate of ammonia, to redissolve the carefully-washed carbonate of lithia in hydrochloric acid, and, again evaporating to dryness and fusing, to redetermine the chlorine by a slightly different method, namely, that of analysis by measure, as applied by Pelouze to the examination of the atomic weights of sodium and barium.

3·9942 grms. of the chloride of lithium thus prepared from the carbonate were dissolved in water. 10·1278 grms. of chemically pure silver (the quantity necessary for the precipitation of the chlorine,

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if Li=89·0, and therefore not quite sufficient for the amount of Cl actually present) were dissolved in pure nitric acid, and the two solutions were mixed in a white glass flask. The mixture was gently heated, and shaken until the chloride of silver had completely separated, leaving the fluid clear. A solution of 1 grm. of pure silver in nitric acid had been prepared, and diluted until the volume =1000 cub. centims., 1 cub. centim. therefore containing 0·001 grm. of silver. This solution was now cautiously added to the fluid in the flask from a pipette furnished with a small glass stopcock and graduated to the one-fifth of a cubic centimetre, the flask being shaken after each addition of the test-fluid until the chloride of silver had completely separated. 42·4 cub. centims. of this dilute solution of nitrate of silver were needed to complete the precipitation of the chlorine=0·0424 grm. of silver.

Hence altogether 10·1278+0·0424=10·1702 grms. of silver had been used.

10·1702 : 3·9942 :: 1349·66 (equiv. of Ag) : x

x=530·06 (equiv. of LiCl).

530·06−443·28 (equiv. of Cl)=86·78=equiv. of Li.

This number agrees sufficiently nearly with those derived from the two former experiments to show that all three are deserving of confidence. If we take the mean of the three, we shall have the number 86·89 for the equivalent of lithium; and this may, I believe, be fairly trusted as a closer approximation to the truth than any of the numbers hitherto received, if we take into account the greater scale upon which the analyses have been made and the difference in the methods pursued. For it will be observed that the effect of the difficulty in determining sulphate of baryta already mentioned (namely the adherence of a little of the salt used for precipitation so as to scarcely permit its removal by washing) will necessarily be to increase the apparent per-centage of sulphuric acid in the sulphate of lithia analysed, and hence to give a *lower* equivalent for the alkali than the true one. But this is the method by which the results hitherto most relied upon have been obtained.

The number 86·89 on the oxygen scale corresponds to 6·95 upon the hydrogen, thus making the equivalent of lithium almost exactly an even multiple of that of hydrogen, in accordance with the analogy which seems to extend further and further through the list of elements, as our knowledge of their atomic weights becomes more exact.

And further, if we take the mean of the equivalents of potassium and lithium, using 86·89 for the latter, we get—

488·86 (Marignac)
86·89

2)575·75

287·87—almost exactly the equivalent of sodium (287·44), as determined by Pelouze.—Silliman's *Journal* for November 1856.

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On Solanine and its Derivatives. *By* A. MOITESSIER.

Many species of the genus *Solanum* (*S. nigrum*, *S. dulcamara*, *S. tuberosum*, &c.) furnish alkaloids which are generally considered as identical; the author has not analysed these substances, but states that in their physical characters they differ sensibly from each other, and that the confusion of these different substances may be the cause of the different formulæ given to solanine. The author's paper refers to the alkaloid of *S. dulcamara*. The following are the results of several analyses of this substance:—

C	60·73	60·73	60·91	
H	8·43	8·39	8·69	
N	..	..	..	3·61

This leads to the formula $C^{42}H^{35}NO^{14}$, which gives by calculation—

C	60·91	14 =	252	61·0
H	8·69	35	35	8·5
N	3·61	1	14	3·4
O	26·79	14	112	27·1

M. Blanchet's formula is very different, $C^{84}H^{68}NO^{28}$. According to him the alkaloid contains—

C	62·0
H	8·9
N	1·6
O	27·5

O. Henry has arrived at the following constitution:—

C=75·00 H=9·14 N=3·08 O=12·78.

To determine the equivalent of solanine in order to establish its formula, the author has deduced it from the analysis of its derivatives, as that of its salts, which are all amorphous and gummy, did not lead to the desired result.

Æthylosolanine is obtained by heating to 248° F. in a sealed tube an alcoholic solution of solanine and iodide of æthyle, and precipitating the product of the reaction by ammonia. Representing solanine by $C^{42}H^{35}NO^{14}$, the formula of æthylosolanine becomes

$$C^{42}H^{34}(C^{4}H^{5})NO^{14}=C^{46}H^{39}NO^{14}.$$

Adopting the formula of M. Blanchet, that of æthylosolanine would be $C^{88}H^{72}NO^{28}$. The analysis of æthylosolanine, compared with the theoretical data furnished by the author's formula and that of Blanchet, is as follows:—

	Experiment.	Calculation ($C^{46}H^{39}NO^{14}$).	Calculation ($C^{88}H^{72}NO^{28}$).
C	62·26	62·58	63·12
H	8·85	8·8	8·59
N	..	3·17	1·67
O	..	25·39	26·62

From these numbers the author thinks the formula $C^{42}H^{35}NO^{14}$ must be adopted for the alkaloid of the *Solanum dulcamara*

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Æthylosolanine is a white substance, apparently amorphous, but under the microscope appears to be composed of a mass of entangled crystals. It is inodorous, bitter, insoluble in water, soluble in alcohol. All the salts are very soluble and gummy; they are very poisonous.

Amylosolanine is obtained like the preceding body, replacing the iodide of æthyle by iodide of amyle; its formula is

$$C^{42}H^{34}(C^{10}H^{11})NO^{14}=C^{52}H^{45}NO^{14},$$

and its salts closely resemble æthylosolanine in their physical and chemical properties.

Æthylamylosolanine is obtained by the action of iodide of amyle upon æthylosolanine or of iodide of æthyle upon amylosolanine. Its formula is

$$C^{42}H^{32}(C^{4}H^{5})(C^{10}H^{11})NO^{14}=C^{56}H^{49}NO^{14}.$$

In its properties it greatly resembles the two preceding bodies.—*Comptes Rendus*, Nov. 17, 1856, p. 978.

Note on Iodized Subacetate of Lanthanium. By A. Damour.

The author has found that the subacetate of lanthanium precipitated from a solution in acetic acid possesses the property of being coloured blue by iodine. For this purpose, the oxide or carbonate of lanthanium is dissolved in an excess of acetic acid, the acid solution is diluted with a large quantity of water, and supersaturated in the cold with ammonia. The subacetate is precipitated in gelatinous semitransparent flakes, which remain for some time suspended in the liquid. As soon as it begins to settle, it is collected on a filter, washed with cold water, and when the greater part of the acetate of ammonia is got rid of, some fragments of iodine are thrown upon the surface of the substance remaining on the filter. A colour, violet at first and then deep blue, appears almost instantly at the point of contact of the grains of iodine, and extends by degrees through the whole mass of the gelatinous hydrate. This effect may be hurried by pouring alcohol over the iodine, which is thus dissolved and carried more rapidly through the mass, which may then be washed with cold water without any fear of removing the colour.

The iodized subacetate of lanthanium preserves its deep blue colour when dried in the cold; the colour disappears at 176° F. It then acquires a yellowish-white or brownish-yellow tint at some points, retaining a considerable proportion of water, which is only evolved at a higher temperature. When dried and decolorized, and heated to incipient redness in a glass tube, it disengages a considerable quantity of water, becomes white, and then carbonized, acquiring a deep black colour. When strongly heated to redness in contact with the air, it becomes brown, and evolves the peculiar odour of vapour of iodine, which is strongly felt only at the moment when the incandescence has just ceased.

When brought to a pasty state by incomplete desiccation, the iodized subacetate of lanthanium is easily diffused in water, and

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remains suspended in it in a state of extreme division, so as to colour the liquid of a deep indigo-blue. The blue colour disappears by long boiling. The subacetate then regains its own white colour. The addition of iodine and a small quantity of ammonia to the liquid in which the decolorized salt is suspended reproduces the blue colour, and the compound settles in blue flakes.

Acetic, muriatic, nitric and sulphuric acids, added to the liquid coloured blue by the subacetate, cause the colour to disappear; ammonia in excess produces the same effect.

To obtain the blue coloration, the oxide of lanthanium employed must be well separated from oxide of cerium, with which it is constantly associated in the mineral kingdom; the solution of the oxide in acetic acid employed by the author had a slight rose-tint, probably from its containing a little oxide of didymium.

The subsalts of lanthanium precipitated by ammonia from their solutions in muriatic, nitric, sulphuric and hydriodic acids, are not coloured blue by iodine.

Alumina, yttria and oxide of cerium, treated in the same way, are not coloured blue by iodine; they only acquire a deeper or paler yellow tint.

The author considers that the blue colour is due not to a combination of the two substances, but rather to a simple diffusion of the iodine between the molecules of the gelatinous salt.—*Comptes Rendus*, Nov. 17, 1856, p. 976.

Investigation of Niobium. *By* R. Hermann.

1. The author has discovered a process by which tantalic acid, when it occurs together with acids of niobium, may be separated from the latter. By the aid of this, he found that the columbite of Bodenmais contains considerable quantities of tantalic acid; he found 31·17 per cent.

This separation depends upon the fact, that, as the author has observed, the A-sulphate of the tantaloid acids of the columbite of Middletown, æschynite and samarscite, dried at 59° F., is decomposed when digested with solution of caustic soda. Soda-salts of the tantaloid acids of these minerals are formed, of which only a very small quantity is dissolved by the solution of soda, whilst by far the greater portion separates from the solution in a crystalline form. If the solution be then poured away from the crystals, and the latter treated with a sufficient quantity of boiling water, they are entirely dissolved.

When the A-sulphate of tantalic acid, from tantalite from Kimito, was treated in the same way, no soda-salt was formed; the tantalic acid also remained almost completely undissolved after the addition of boiling water.

By the digestion of the A-sulphate of the metallic acids of the columbite of Bodenmais, soda-salts were certainly formed; but on the addition of boiling water these were not completely dissolved. With this first treatment, 26 per cent. of the weight of the acid,

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tantalic acid, employed in the experiment remained undissolved. The dissolved soda-salts were precipitated by muriatic acid and ammonia, and the acids thus separated were again converted into A-sulphate by fusion with sulphate of potash and washing. After a second digestion of this A-sulphate with solution of soda, and dissolving the soda-salts thus formed in boiling water, there only remained 5·17 per cent. of tantalic acid undissolved. By a third exactly similar treatment soda-salts were obtained, which dissolved entirely in water.

Therefore from 100 parts of the metallic acids from the columbite of Bodenmais, 31·17 parts of tantalic acid were obtained. The tantalic acid thus obtained agreed completely with the ordinary acid in its behaviour before the blowpipe and with reagents.

2. *Upon Niobic Acid, Pelopic Acid, Ilmenous Acid, and Ilmenic Acid.*—It is well known that Rose, after first of all concluding from the behaviour of the chlorides of niobium that they belonged to two different metals, subsequently ascertained that they belonged to one and the same metal, so that pelopium was dropped. Rose has also expressed doubts regarding ilmenium. Hermann has now found that his ilmenous and ilmenic acids are nothing but niobic acid. Consequently we must take the relations of the bodies hitherto known as tantaloid acids in the following way:—

Tantalic acid is	Ta^2O^5
Pelopic acid is a mixture of tantalic acid and niobate of niobous acid ..	$Nb^2O^5, NbO^2 + xTa^2O^5$
Ilmenic acid is niobate of niobous acid	Nb^2O^5, NbO^2
Ilmenous acid is sesquiniobate of niobous aid	$(Nb^2O^5)^2NbO^2$
Niobic acid is niobous acid	Nb^2O^5

3. *Behaviour of Niobium towards Muriatic Acid; separation of Niobous Acid from Niobate of Niobous Acid.*—Niobous acid is completely soluble in muriatic acid of spec. grav. 1·160, but almost entirely insoluble in acid of 1·094. Niobate of niobous acid is dissolved by muriatic acid of 1·094. Mixtures of the two bodies may therefore be separated by treatment with muriatic acid of spec. grav. 1·094.

A very certain process for dissolving the acids of niobium in muriatic acid is the following:—20 grms. of these acids are brought to a red heat and a fluid state with an excess of hydrate of soda, and the salt put into 30 oz. of boiling water. A perfectly clear solution of the soda-salt is produced. This solution is mixed with an excess of nitric acid, and the fluid is then supersaturated with ammonia, in order to be able to filter it more easily. The precipitate is put upon a filter, and allowed to drip, but not washed. The precipitate, whilst still moist, but well drained, is well stirred with 5 oz. of muriatic acid, of spec. grav. 1·160 at least, during which care must be taken that no lumps remain; the acid mixture is heated in a spacious glass flask, and 24 oz. of boiling water are added to the boiling fluid. A perfectly clear solution of the acids of niobium in muriatic acid will now be obtained.

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To separate niobate of niobous acid from niobous acid, the process is exactly the same, only that instead of muriatic acid of spec. grav. 1·160, one of 1·094 is employed. In this way niobate of niobous acid (Nb^2O^3, NbO^2) is dissolved, and niobous acid remains undissolved, but this obstinately retains some niobate of niobous acid. To determine this last intermixture, crystallized soda-salts must be prepared with this impure niobous acid, from the amount of soda in which the intermixed niobate of niobous acid may be calculated. Pure niobite of soda contains 19·53 per cent. of soda, whilst the soda-salt of the two acids contains 24·06 per cent. of soda. The niobous acid separated by muriatic acid, however, gives soda-salts, whose amount of soda varies between 20 and 22 per cent.

4. *Atomic Weight of Niobium.*—The author has deduced this from the determinations of the acid, and of the soda of the soda-salts, and of the chlorine in the chlorides. The numbers vary in some determinations between 648·60 and 664·10, and give on an average Nb=655·1.

5. *On Niobium and its Compounds.*—Niobium is obtained by heating protochloride of niobium in a current of ammoniacal gas; it forms a black powder of the appearance of silicium. It ignites when heated, and smoulders away like tinder, forming white niobous acid. There are the seven following oxides of niobium:—

Brown Oxide of Niobium, NbO^x, is produced by the action of zinc upon solutions of niobic acid in muriatic acid, in the absence of air. Its composition is still unknown.

Violet Oxide of Niobium, Nb^4O^5 or $2NbO, Nb^2O^3$, with an amount of oxygen found of 15·90 per cent., is produced by the calcination of niobous acid in an air-tight crucible filled with charcoal at the temperature of melting iron.

Blue Oxide of Niobium, NbO^x.—Composition unknown. Produced in the ammoniophosphate of soda test by the calcination of niobous acid, and the treatment of the compounds of this acid with muriatic acid and zinc, colouring the solutions transitorily of a fine blue.

Niobous Acid, Nb^2O^3, is produced,—1st, by decomposing the white protochloride of niobium with water; and 2ndly, by the oxidation of the brown oxide by the oxygen of the air; the latter method is the most advantageous. Spec. grav. 5·0 or 5·09. It colours the ammoniophosphate of soda violet when treated in the inner flame; and after the addition of an excess of niobous acid, fine pure blue, by the formation of violet and blue oxides. The other acids of niobium never give these reactions, nor do they furnish blue, but always brown glasses. It contains 18·63 of oxygen for 81·37 of niobium.

Sesquiniobate of Niobous Acid, Nb^5O^8 or $2Nb^2O^3+NbO^2$, is produced,—1st, by the decomposition of sesquiniobous chloride of niobium with water; and 2ndly, by the fusion of samarscite with bisulphate of potash, washing, purifying, and calcining the A-sulphate remaining undissolved. Contains 80·37 Nb and 19·63 O.

Niobate of Niobous Acid, Nb^2O^3, NbO^2, is obtained,—1st, by the

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decomposition of the yellow niobous chloride of niobium with water; 2ndly, by boiling mixtures of niobic and niobous acids with muriatic acid of spec. grav. 1·094, when the niobate of niobous acid dissolves in the muriatic acid; and 3rdly, by fusing æschynite with bisulphate of potash and washing, when A-sulphate of the niobiate of niobous acid remains undissolved. This acid is distinguished from the others especially by its solubility in muriatic acid of spec. grav. 1·094, by the dark brown colour communicated to it by the ammoniophosphate of soda, which is darker than that of sesquiniobate of niobous acid, and by its less specific gravity=3·95 to 4·30. Moreover it gives peculiar salts with soda, which either correspond with the formula $3(NaO\ Nb^2O^3) + (NaO)^2, 3NbO^2$ or $NaO\ Nb^2O^3 + NaO\ NbO^2$. The former salt contains 20·94, the latter 24·09 per cent. of soda.

Niobic Acid, NbO^2, is unknown in the pure state. The author only concludes that it exists because,—1st, in pyrochlore, yttroilmenite and æschynite, titanic acid occurs, which partially displaces the niobium acid, and titanic acid can only displace an acid of the formula NbO^2; and 2ndly, he found an acid in yttroilmenite, which was quite different from the previously-described lower grades of oxidation, and gave a soda-salt with 28·30 per cent. of soda. An acid of the formula NbO^2 must saturate 31·37 per cent. of soda, which the author therefore regards as sufficiently concordant.

Chlorides of Niobium.—Besides the oxychlorides, the author adopts the three following chlorides of niobium. The preparation of the first and third is well known:—

White Niobous Chloride, Nb^2Cl^3, is a white spongy mass, emitting fumes of muriatic acid in the air, and becoming converted into mixtures of niobous acid and oxychloride of niobium. It dissolves completely in a sufficient quantity of boiling muriatic acid of spec. grav. 1·60. When niobous chloride is thrown into water, a hissing sound is produced, as by the immersion of a red-hot body in water. Composition:—

	Calculated.	From acid of æschynite.	From acid of samarscite.	From acid of pyrochlore.
2Nb=1310·20	49·63	49·76	49·74	49·87
3Cl 1329·84	50·37	50·24	50·26	50·13

Sesquiniobous Chloride of Niobium, $2(Nb^2Cl^3) + NbCl^2 = Nb^5Cl^8$, is obtained according to the following prescription:—A mixture of 2 parts of yellow and 1 part of white chloride of niobium is put into one end of a glass tube of sufficient length and width, a piece of the glass tube in front of the mixture is first heated to redness, and the mixture is then driven by heat, with the assistance of a current of dry carbonic acid, over this red-hot part of the glass tube. In this way the yellow chloride disappears for the most part, and globular aggregations of small, silky, prismatic crystals of sesquiniobous chloride of niobium sublime into the cold part of the tube.

Forms globular and also asbestos-like aggregations of small, white, silky, prismatic crystals. Behaviour towards muriatic acid and water same as that of niobous chloride. Decomposed by water into

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muriatic acid and sesquiniobate of niobous acid. This compound consists of—

5Nb =	3275·50	48·02	47·98
8Cl	3546·24	51·98	52·02

Yellow Niobous Chloride of Niobium, $Nb^2Cl^3 + NbCl^2 = Nb^3Cl^5$, yellow prisms, which fuse at a gentle heat to form yellow drops, and volatilize in the form of white chloride of niobium at a much lower temperature. In the air it emits fumes of muriatic acid, becomes rapidly white and converted into niobate of niobous acid and oxychloride of niobium. It is perfectly soluble in boiling muriatic acid, and is completely converted by water into niobate of niobous acid. Composition:—

		Calculated.	From acid of æschynite.	From acid of columbite from Bodenmais.
3Nb =	1965·3	47·00	47·00	46·59
5Cl	2216·4	53·00	53·00	53·51

Sulphuret of Niobium, $(NbS)^3 + Nb^2S^3$, consisting of 26·03 of sulphur and 73·97 of niobium, is obtained by the calcination of the acids of niobium in vapour of sulphuret of carbon.

Compounds of Niobic Acids with Sulphuric Acid.—In the compounds of sulphuric acid with the acids of niobium, these appear in three different states, which the author indicates by A, B and C.

The A-sulphates are produced when the acids of niobium are brought to a clear fluid state with 6 times their quantity of bisulphate of potash, and the acid salt washed with water.

The B-sulphates are produced when solutions of the acids of niobium in strong muriatic acid are mixed with sulphate of potash, and the precipitate pressed out between bibulous paper without washing.

The C-sulphates are formed when acids of niobium are fused together with a great excess of hypersulphate of potash or ammonia, and the acid masses dissolved in water. Opalescent solutions are formed, which become turbid when heated to boiling, when the C-sulphates separate as transparent precipitates, similar to alumina. These precipitates are collected by filtration, and well pressed, but not washed, as by that means they lose sulphuric acid.

The analysis of the compounds of the acids of niobium with sulphuric acid is effected in the following manner:—A portion of the compound is exposed to a strong red heat, and the loss of water and sulphuric acid observed. Another portion of the same compound is fused with hydrate of soda, the saline mass is dissolved in water, and the fluid mixed first with muriatic acid in excess, and afterwards with ammonia, also in excess, after which the separated acids of niobium are collected on a filter and well washed. The fluid drained away from this precipitate now contains all the sulphuric acid which was combined with the acids of niobium; this may be determined by precipitation with a baryta-salt.

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In this way the author has prepared and analysed the following salts:—

A-*Sulphate of Niobous Acid*, $(Nb^2O^3)^9 + SO^3 + 22HO$, forms white chalky fragments. Analysis:—

Nb^2O^3	83·00	9 =	14491·80	82·97
SO^3	2·96	1	500·75	2·86
HO	14·04	22	2475·00	14·17

A-*Sulphate of Niobate of Niobous Acid*, $(Nb^2O^3)^9\,SO^3 + 3[(NbO^2)^3\,SO^3] + 52HO$, obtained by the fusion of Nb^2O^3, NbO^2 with bisulphate of potash, washing, &c., is exactly similar to the preceding salt. Analysis:—

Nb^2O^3 } NbO^2	73·940	73·220	9 } 9 =	22187·70 73·87
SO^3	6·405	7·226	4	2003·00 6·66
HO	19·655	19·574	52	5850·00 19·47

B-*Sulphate of Niobous Acid*, $(Nb^2O^3)^2\,SO^3 + 5HO$.—Niobous acid is dissolved in strong muriatic acid, precipitated by sulphate of potash, and pressed between blotting-paper without washing or drying. A white powder, which loses sulphuric acid by washing. Analysis:—

Nb^2O^3	75·00	2 =	3220·40	75·18
SO^3	11·94	1	500·75	11·69
HO	13·06	5	562·50	13·13

C-*Sulphate of Niobous Acid*, $(Nb^2O^3)^2, 5SO^3 + 10HO$.—Obtained as a precipitate by fusing niobite of soda with a great excess of hypersulphate of ammonia, dissolving the clear saline mass in cold water, and heating the opalescent fluid to boiling. This precipitate is only pressed between bibulous paper. It is an alumina-like precipitate drying into horny pieces, which swell up when heated into an amber-like mass, and when strongly heated lose their sulphuric acid. Analysis:—

Nb^2O^3	47·73	2 =	3220·40	47·01
SO^3	36·55	5	2503·75	36·57
HO	15·72	10	1125·00	16·42

C-*Sulphate of Niobate of Niobous Acid*, $2(Nb^2O^3, SO^3) + (NbO^2)^3, SO^3 + 16HO$, is prepared the same way as the preceding salt, and has the same properties, but the fragments are not inflated when heated to redness. Analysis:—

Nb^2O^3 } NbO^2	53·49	2 } 2 =	4930·60
SO^3	26·84		2503·75
HO	19·67		1800·00

6. *Soda-Salts of Niobic Acid.*—They can be prepared by boiling their still-moist A-sulphates with solution of caustic soda, or by fusing the dry acids with hydrate of soda. The author has obtained the following soda-salts:—

Niobite of Soda, $NaO, Nb^2O^3 + 5HO$.—Obtained by fusing nio-

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bous acid with hydrate of soda, dissolving in water and crystallizing. From dilute solutions the salt crystallizes with 7 atoms of water. When anhydrous it contains—

	From acid of columbite from Bodenmais.	From acid of columbite from Middletown.	From acid from Samarscite.			
Nb^2O^3	80·68	81·06	80·22	1 =	1610·2	80·47
NaO	19·37	18·94	19·78	1	390·9	19·53

Sesquiniobic Niobite of Soda, $2(NaO, Nb^2O^3)+NaO, NbO^2$ (dried).—Crystals which become turbid in the air. Obtained by fusing the double acid with hydrate of soda.

Acid Niobic Niobite of Soda, $2(NaO, Nb^2O^3)+2NaO, 3NbO^2+35HO$, and neutral salt, $NaO, Nb^2O^3+NaO, NbO^2+xHO$.—The acid salt forms silky prisms; the neutral, which was obtained with 13 and 18 atoms of water, formed laminar aggregations in both cases.

7. *Niobite of Potash*, obtained by fusing the acid with hydrate of potash, of the formula $2KO, 3Nb^2O^3+12HO$, with 18·91 per cent. of water, separates in radiate aggregations only on the drying of the syrupous solution.—*Journ. für Prakt. Chem.*, lxviii. p. 65.

Experiments on the comparative Solubility of Mixtures of Salts. By Dr. F. Pfaff.

The author has made some experiments upon the modifications presented by the solubility of salts when several of them are taken up by one and the same solvent. To avoid supersaturation, all the salts which occur in the two series of experiments made by the author were dissolved in water cooled to 32° F., with which they remained in contact for twenty-four hours, with occasional stirring. Care was taken that the temperature of the water should not rise above 34° F According to the experiments which the author originally made with a view to geological investigations, 100 parts of water at 32° F. dissolve—

Sulphate of soda, NaO, SO^3	5·175
Sulphate of magnesia, MgO, SO^3	28·067
Sulphate of copper, CuO, SO^3	15·103

After the solubility of these salts by themselves had been determined, the author investigated the mixtures which these salts furnish by combination. Of these, four are possible. In the following numbers the solubilities always refer to 100 parts of water at 32° F.

1. Sulphates of copper and soda:—

CuO, SO^3	8·038	Sum,
NaO, SO^3	6·311	14·349

2. Sulphates of magnesia and soda:—

MgO, SO^3	15·306	Sum,
NaO, SO^3	13·086	28·392

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3. Sulphates of magnesia and copper:—

MgO, SO^3	23·914	Sum,
CuO, SO^3	6·559	30·473

4. Sulphates of copper, magnesia and soda:—

CuO, SO^3	7·169	Sum,
MgO, SO^3	21·319	35·318
NaO, SO^3	6·830	

From these the following facts are deduced:—

1. 100 parts of water sometimes dissolve more and sometimes less of different salts than of one alone.

2. The salts usually lessen their solubility mutually; only NaO, SO^3 dissolves in larger quantities in mixtures than by itself.

3. The diminution and the increase stand in no recognizable connexion either with the atomic weight or with the general solubility, or with the faculty of taking up water in crystallizing; they follow no law recognizable at present.

The employment of sulphate of potash instead of sulphate of soda in the above mixtures gave exactly similar results, but in this case an increased solubility appeared when it was mixed with other salts.

In all cases in the preceding series, saturated solutions were operated with. As it was the author's principal object to acquire information as to the relations of solubility occurring in nature when water penetrates into rocks and carries out some of their constituents, he also made the following experiments, which show in what proportions the individual salts are dissolved from various saline mixtures, under the condition that the solution cannot attain saturation.

The mixtures of the same four combinations of the salts above mentioned were put into glass tubes, 12 millims. in width, closed beneath with filtering paper, until the tubes were about one-tenth filled with them. An arrangement was contrived by which the apparatus was constantly kept at 32° F., and the water was also cooled to 32° F. The following are the results:—

1. *Mixtures of Sulphates of Copper and Soda.*—The water ran very quickly through them, in five minutes rather more than 14 grms. 100 parts of this water contained 9·480 of salts, consisting of—

CuO, SO^3	3·880	Sum,
NaO, SO^3	5·600	9·480

Calculated for the saturated solution of 14·349, this gives—

CuO, SO^3	5·880 instead of 8·038
NaO, SO^3	8·469 instead of 6·311

2. *Mixtures of Sulphates of Magnesia and Soda.*—In half an hour 10·276 grms. of fluid were filtered off. They contained in 100 parts—

MgO, SO^3	4·767	Sum,
NaO, SO^3	7·218	11·985

Calculated for 28·392:—

MgO, SO^3	11·295 instead of 15·306
NaO, SO^3	17·097 instead of 13·086

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3. *Mixtures of Sulphates of Magnesia and Copper.*—The water filtered through very slowly; in three hours 9·646 grms. of solution had flowed through. This contained in 100 parts of water—

MgO, SO^3	3·368	Sum,
CuO, SO^3.....	3·088	6·456

Calculated for 30·473:—

MgO, SO^3.....	15·866 instead of 23·914
CuO, SO^3	14·607 instead of 6·559

4. *Mixtures of Sulphates of Copper, Magnesia and Soda.*—The water ran through pretty quickly; in a quarter of an hour 14 grms. had passed. These contained in 100 parts of water—

CuO, SO^3	2·770	Sum,
MgO, SO^3.....	4·456	14·031
NaO, SO^3	6·805	

Calculated for 35·318:—

CuO, SO^3.....	6·972 instead of 7·169
MgO, SO^3	11·216 instead of 21·319
NaO, SO^3.....	17·130 instead of 6·830

In this series, as in the preceding, it is the sulphate of soda that dissolves most rapidly and easily. The quantity of a salt which is dissolved by the long action of water upon it, gives no rule for the facility with which it is extracted by water from saline mixtures; the presence or absence of other salts modifies this proportion considerably. Even with an excess of water, the salts do not dissolve in the proportions of their absolute solubility when they are extracted from mixtures with other salts.—Liebig's *Annalen*, xcix. p. 224.

On the Action of Perchloride of Phosphorus upon the fixed Organic Acids. *By* Lies Bodart.

If 2 equivs. of pentachloride of phosphorus be heated with 1 equiv. of mucic acid in a retort, not higher than 320° F., muriatic acid is evolved in abundance; and if it be removed from the fire at the time when the mass begins to become brown, and the excess of chloride of phosphorus be decomposed by the addition of water after cooling (during which the mass must be cooled), the fluid contains a chlorinated acid. To obtain this, the fluid is saturated with milk of lime, by which the phosphoric and muriatic acids produced are neutralized; it is then left to crystallize. The lime-salt of the acid is obtained in the form of verrucose aggregations of crystals.

By mutual decomposition with acetate of lead, this salt furnishes the lead-salt of the acid, from which the lead may be thrown down by sulphuretted hydrogen.

The acid is $=C^{12} H^2 Cl^2 O^6 + 2HO$.
The silver-salt $=C^{12} H^2 Cl^2 O^6 + 2AgO$.

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The formation of this acid is shown by the equation

$$C^{12} H^{10} O^{16} + 2PCl^5 = 2PO^2 Cl^3 + 2HCl + 4HO + C^{12} H^4 Cl^2 O^8.$$

If pyromucic acid, $C^{10} H^4 O^6$, be treated in the same way with pentachloride of phosphorus, we obtain—

$$C^{10} H^4 O^6 + PCl^5 = PO^2 Cl^3 + HCl + C^{10} H^3 ClO^4.$$

The *chloride of pyromucyle*, $C^{10} H^3 ClO^4$, thus obtained, is fluid, strongly refractive, boils at 338° F., smells like chloride of benzoyle, and strongly provokes tears. If this body be placed under a bell-glass with a cup of water, it is volatilized, and the water contains regenerated mucic acid. With ammonia it immediately produces pyromucamide. These two conversions are—

1. $C^{10} H^3 ClO^4 + 2HO = HCl + C^{10} H^3 O^5 HO.$
2. $C^{10} H^3 ClO^4 + NH^3 = HCl + C^{10} H^5 NO^4.$

Malic acid also underwent an alteration by this treatment, but took up no chlorine. The author has not yet exactly ascertained the nature of the decomposition which takes place in this case.—*Comptes Rendus*, xliii. p. 391.

On the Colouring Matter from Monarda didyma.
By M. Belhomme.

The author states that the flowers of *Monarda didyma*, Linn. (*Monarde écarlate*) contain the same colouring matter as the fruits of the nopal and cochineal, and that they may be employed with advantage in the preparation of carmine.—*Comptes Rendus*, xliii. p. 382.

PROCEEDINGS OF SOCIETIES.

Royal Society.

May 22, 1856. (The Lord Wrottesley, President, in the Chair.)

"On some of the Products of the Distillation of Boghead Coal at low temperatures." By C. Greville Williams, Esq.

In presenting a brief preliminary notice of an investigation of the substances obtained by distilling boghead coal at low temperatures, I may observe that I was induced to undertake it from remarking the low density of the naphtha produced in the process; it being only ·750 at 60° F., although its boiling-point, previous to the rectifications, was as high as 290° F.

After fifteen complete fractionations of the portion distilling below 310° F., boiling-points were obtained as low as 170°, and it was found that the fluid could be separated, by careful treatment with fuming nitric, or a mixture of nitric and sulphuric acids, into two bodies, one forming a nitro-compound, the other being unacted on. The latter was washed several times with a strong alkaline solution, and, after being digested for a few days with sticks of potash to

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remove adherent moisture, rectified over sodium. In this manner I obtained a colourless and very mobile fluid with a pleasant odour, distantly resembling that of hawthorn blossoms. Its density at 60° was ·725.

I selected the fraction boiling in the fifteenth rectification at 240° F. to make a preliminary experiment upon, and, after purification in the manner described, it gave in three perfectly concordant analyses, exactly the per-centage of carbon and hydrogen required for butyle (valyle of Kolbe), the radical of the butylic alcohol. Two determinations of the vapour density, taken respectively at 80° and 107° above its boiling-point, gave numbers closely coinciding with theory.

When it is considered that 68° or more of difference of boiling-point only cause a variation of 0·3 in the per-centage of carbon and hydrogen of bodies of this class, it becomes evident that if I had taken the fraction boiling at 223° (Wurtz) or 226° (Kolbe), it would have yielded the same results. This point is now under examination.

The formula

$$C^{16}H^{18}=4 \text{ vols.},$$

corresponds not only to butyle, but also to the hydruret of caprylyle, and, of course, both these bodies have the same vapour density; but several circumstances lead me to believe the hydrocarbon I have obtained to be the radical of the butylic alcohol. The density of the fluid, and the temperature at which it distils, are also rather in favour of this view. It will be seen that 243° F. should be the boiling-point of butyle if Frankland's determination of that of amyle be correct, and Kopp's law hold with these bodies.

A careful study of the papers already published on the radicals of this series, shows that more than one anomaly appears to exist in their physical properties, the gradations usually observed in homologous groups not being so distinctly marked as with most others, and this fact somewhat impedes their identification. The large quantity of substance which becomes at our disposal from the source mentioned, will, by facilitating the study, throw light on these points.

I believe I shall be able to isolate at least four of the radicals, viz. propyle, butyle, amyle, and caprotyle, from the coal distillate. The per-centage composition varying so little with the different homologues, I rely chiefly on vapour density and products of decomposition as the means of proving their presence.

The hydrocarbons accompanying the radicals are also quite distinct from the benzole series, as shown by the low density of the nitro-compound. The latter is extremely difficult of reduction by sulphide of ammonium or protacetate of iron, but it furnishes a volatile oily alkaloid by distillation with an alcoholic solution of potash.

The tedious purifications and the numerous operations required before the substances can be obtained in a state of sufficient purity for analysis from the coal distillate, will probably cause a considerable period to elapse before a detailed account of all the bodies can be published.

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THE CHEMICAL GAZETTE.

No. CCCXLII.—January 15, 1857.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Production of Carbonic Acid by the Decomposition of Organic Matters. *By* B. CORENWINDER.

THE author describes a series of experiments made with a view to ascertain the quantities of carbonic acid which are produced by the decomposition of organic matters, manures, &c. in the soil.

First Experiment.—On the 12th of June 1851, a flowerpot was filled with garden-earth (clay-soil which had not been manured for a long time) composed of

31·90 water,
13·70 organic matter,
54·40 mineral constituents,

and placed under a bell-glass connected with an aspirator and the apparatus necessary for determining the carbonic acid formed, as carbonate of baryta. The earth formed a layer of 50 square centims. in surface and 8 centims. in height.

In twenty-four hours 0·22 grm. of carbonate of baryta were formed, showing an evolution of 0·05 grm., or 25 cub. centims. of carbonic acid. From this it appears that a surface of 1 hectare* of the same soil with a thickness of 8 centims., furnishes 500 hectolitres of carbonic acid in twenty-four hours.

Second Experiment.—On the 1st of July 1851, a pot of the same size, filled with a more argillaceous earth, was put under the bell-glass.

In twenty-four hours, 0·13 grm. of carbonate of baryta, or 14·6 cub. centims. of carbonic acid, were obtained. This amounts to 300 hectolitres on 1 hectare of land.

Third Experiment.—On the third day the soil was broken up with a knife, in order to imitate as far as possible on a small scale the loosening of the soil by field-work. In twenty-four hours 0·17 grm. of carbonate of baryta was obtained=19·3 cub. centims. of carbonic acid. This amounts to 400 hectolitres per hectare.

Fourth Experiment.—Earth from a cultivated beet-field on which clover had been previously raised. The earth was employed in a

* The *hectare* is somewhat less than 2½ English acres; the *hectolitre* a little more than 3½ cubic feet.—ED.

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quantity of 63·3 square centims. in surface, with a depth of 8 to 9 centims. It consisted of

12·50 water,
4·80 organic matter,
82·70 mineral constituents.

The field had received 3·3 kilogrms. of stable-manure and rape-cake per hectare the winter before. The earth was clayey, and contained no carbonate of lime. The mass of rape-cake was already in an advanced state of decomposition. The experiment lasted for four days. In twelve hours there were obtained—

First day.....	0·505,	Third day	0·450,
Second day....	0·470,	Fourth day	0·400,

of carbonate of baryta, or an average of 0·912 of carbonate of baryta in twenty-four hours. The temperature during these days was 68° to 77° F., at noon 86° to 95° F.

The temperature has no very great influence within such small variations; at least its influence is compensated by the drying of the soil and the organic matter contained in it.

The result of this experiment therefore shows that on an average 0·202, or about 100 cub. centims. of carbonic acid, are produced from the pot, and 1·570 hectolitres from the hectare of land.

On the whole, these quantities of carbonic acid are much more considerable than has been supposed. They are not equal in the experiments, because the quantity is greater in proportion to the amount of organic matter in the soil, and the ease with which this is decomposed.

Fifth Experiment.—Fresh cow-manure was placed under the bell-glass for twenty-four hours at 68° F. In twenty-four hours, 0·545 of carbonate of baryta, or 62 cub. centims. of carbonic acid, were obtained from a layer of 50 square centims. and 8 centims. in depth. This gives 1240 hectolitres per hectare. The next day, 0·525 grm. of carbonate of baryta was obtained.

The same mass was then kept for four days, and again submitted to experiment. In twenty-four hours, with a temperature of 73° to 77° F., 1·125 grm. of carbonate of baryta, or 126 cub. centims. of carbonic acid, were obtained. The pot had a surface of 63·3 square centims.; the depth of the layer was 8 centims. A hectare of manure of the same nature would therefore furnish 2000 hectolitres of carbonic acid in twenty-four hours.

Seventh Experiment, with Cow-dung.—In twenty-four hours, 0·525 grm. of carbonate of baryta were obtained, or about 1200 hectolitres of carbonic acid for a surface of 1 hectare.

Eighth Experiment, with Horse-dung.—The quantity of carbonic acid obtained in this case on the first day of the experiment, with fresh horse-dung, for a stratum of 8 centims. in thickness and 1 hectare in surface, amounted to 500 hectolitres.

The mass was kept for four days. The manure now began to ferment, and furnished such a quantity of carbonic acid, that the experiment could only be allowed to continue for six hours. 0·975

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grm. of carbonate of baryta were obtained, or 440 cub. centims. of carbonic acid, calculated for a period of twenty-four hours and for a surface of 50 square centims. This amounts to 8800 hectolitres per hectare.

Experiments were made with various other organic matters. Sugar, cotton, and moist guano produced very little carbonic acid; on the contrary, the author obtained a great deal of carbonic acid by putting flax moistened with water under the bell-glass.

On the whole, it appears from these experiments that the quantity of carbonic acid produced at the surface of the earth by the decomposition of plants, and thus presented to growing plants, arises for the most part from the decomposition of organic matters; the quantity produced by the respiration of animals, by volcanoes and fires, on the other hand, is inconsiderable in comparison. The plant exists in a sea of carbonic acid, which receives a constant increase by the putrefaction of organic matters.—*Ann. de Chim. et de Phys.*, 3 sér. xlviii. p. 179.

On some Products of Metamorphosis of Hypogæic Acid.
By G. C. Caldwell *and* A. Gössmann.

By the dry distillation of hypogæic acid, discovered in 1855 by Scheven and Gössmann, the authors have obtained ordinary sebacic acid, $C^{20}H^{18}O^8$.

By the action of nitrous acid upon hypogæic acid, a new acid, isomeric with it, is produced. This is

Gaidic Acid, $C^{32}H^{30}O^4$.—It is obtained from the mass treated with nitrous acid, by pressing it to remove an oleaginous mass, and crystallizing the residue from alcohol, until it has become perfectly white and shows a constant melting-point.

It is a colourless, inodorous, crystalline body, with a melting-point of 100° F. The fused substance solidifies in a radiate crystalline mass; it volatilizes at a higher temperature, dissolves readily in æther and alcohol, is insoluble in water, and undergoes no alteration at ordinary temperatures. Analyses:—

C	75·57	75·39	75·41	32	75·59
H	11·98	11·88	12·05	30	11·81
O	..	..	..	4	12·60

The *soda-salt* is obtained by dissolving gaidic acid in an aqueous solution of carbonate of soda. This is evaporated to dryness, and the residue extracted with absolute alcohol. Carbonate of soda remains in the residue. The solution forms a transparent, gelatinous mass on cooling. The salt separates in crystalline laminæ from the evaporated solution.

The *copper-salt*, $C^{32}H^{29}O^3$, CuO, is precipitated from a mixture of a solution of the soda-salt with one of sulphate of copper, in the form of a bluish-green, slightly crystalline compound, which is very difficult of solution in alcohol, and separates from this solution in

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granular crystalline masses. The salt is insoluble in water, and fuses without decomposition at a little above 248° F. Analysis:—

C	67·24	32	67·36
H	10·27	29	10·17
O	..	3	8·42
CuO	13·83	1	14·03

The *silver-salt*, $C^{32} H^{29} O^3$, AgO, obtained in the same way as the copper-salt, by means of nitrate of silver, is a white amorphous powder, insoluble in water, alcohol and æther; when heated with these fluids, it becomes black.

The *æther*, $C^4 H^5 O$, $C^{32} H^{29} O^3$, is produced by passing muriatic acid gas into the solution of the acid in absolute alcohol, slightly digesting the mixture for twelve hours, and then separating the æther by means of water. It is thrown down at first mixed with some unchanged acid. It is therefore dissolved repeatedly in alcohol, and precipitated from this solution by water. It is dried at the temperature of the water-bath in a current of hydrogen.

It is a colourless and inodorous body at 48° to 50° F., solid at a lower temperature; when obtained from the alcoholic solution, it forms laminar crystals, lighter than water, volatilizable without alteration. Analysis:—

C	76·37	36	76·59
H	12·19	34	12·05
O	..	4	11·36

According to this, gaidic acid differs considerably in several points from hypogæic acid. Hypogæic acid and its compounds are changed by exposure to the air. The acid itself and its æther cannot be distilled unchanged.

Gaidic acid, on the contrary, is unalterable in the air, and with its æther may be volatilized without decomposition. The æther of this acid becomes solid at 48° to 50° F., whilst that of hypogæic acid does not become solid even at 14° F. On the other hand, the two acids differ less even in regard to their melting-points. Gaidic acid fuses at 100° F., hypogæic acid at 91° to 93° F.

In conclusion, the authors remark tha tHofstädter's physetoleic acid, which also has the formula $C^{32} H^{30} O^4$, must not at present be regarded as identical with hypogæic acid, as it neither furnishes sebacic acid nor an isomeric acid.—Liebig's *Annalen*, xcix. p. 305.

On the Arachines. *By* M. Berthelot.

In their memoir on the constituents of the oil of *Arachis hypogæa*, Scheven and Gössmann have described an acid of the formula $C^{40} H^{40} O^4$. Berthelot has now prepared the glycerine compounds of arachic acid, the arachines, namely

1. Monarachine.. $C^{46} H^{46} O^8 = C^{40} H^{40} O^4 + C^6 H^8 O^6 - 2HO$,
2. Diarachine.... $C^{86} H^{86} O^{12} = 2C^{40} H^{40} O^4 + C^6 H^8 O^6 - 2HO$,
3. Triarachine .. $C^{126} H^{126} O^{16} = 3C^{40} H^{40} O^4 + C^6 H^8 O^6 - 2HO$,

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and has thus consequently confirmed the formula established by Scheven and Gössmann for arachic acid.

Monarachine is obtained when arachic acid is heated with glycerine to 356° F. at the utmost, for eight hours. It is isolated, and purified with lime and æther.

It is a neutral white body, almost insoluble in cold, and slightly soluble in boiling æther, from which it is deposited in a finely granular state.

Diarachine is obtained,—1st, when glycerine and arachic acid are heated for six hours to 392°–437° F.; or 2ndly, when monarachine is heated for eight hours to the same temperature with arachic acid and a trace of water. It is extracted by means of lime and æther.

A white mass, nearly insoluble in cold, and slightly soluble in boiling æther, from which it separates in extremely fine granules, which exhibit no trace of crystallization even under a strong magnifying power. More soluble in sulphuret of carbon than in æther. From this solution also it is not obtained in distinct crystals. It fuses at 167° F. Heated upon platinum foil, it volatilizes without leaving any ash.

Heated to 212° F. for seventy hours with slaked lime, it becomes saponified, and again produces glycerine and arachic acid.

As in the first mode of preparation diarachine is produced so nearly under the same conditions under which Scheven and Gössmann prepared arachine, and it is almost certain that those chemists must have obtained a mixture of diarachine with arachic acid, the author determined how much free arachic acid is contained in the crude product of the treatment of that acid with glycerine. In 100 parts of the crude fat he found—

Free arachic acid	42·6
Diarachine.....	57·4

The determination was effected as follows:—

0·200 grm. of the crude fat was dissolved in boiling alcohol; litmus, and then normal lime-water, were added until the redness which was communicated to the litmus by the free arachic acid was permanently changed to blue. The quantity of lime employed serves for the calculation of the free acid.

Triarachine is obtained by fusing diarachine with 15 to 20 times its weight of arachic acid. The perfectly dry mixture is put into a tube, and heated for eight to ten hours to 392°–428° F. The triarachine produced is purified with lime and æther.

A neutral body, similar to the preceding, and like them very slightly soluble in æther.—*Ann. de Chim. et de Phys.*, 3 sér. xlvii. p. 855.

On the Formation of Crystallized Sulphocyanide of Silver.

By A. GÖSSMANN.

Experiments on the reactions of oxide of silver upon sulphocyanide of ammonium, gave occasion to the observation of the following very beautiful mode of formation of sulphocyanide of silver. If

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freshly precipitated oxide of silver be digested at a gentle heat with a solution of sulphocyanide of ammonium, a continual evolution of ammonia takes place, whilst oxide of silver is dissolved; and thus a compound of the sulphocyanides of silver and ammonium is formed, together with unchanged sulphocyanide of ammonium. All the sulphocyanide of ammonium could not be converted into the double salt even by long digestion. There still remained so much excess of sulphocyanide of ammonium in solution, that it did not begin to grow turbid by the separation of sulphocyanide of silver until it was diluted with large quantities of water, and even then only after some time. Dr. Caldwell, who performed the experiments at my request, found, as Hull had already ascertained for the corresponding compounds of potassium and sodium*, that the double sulphocyanide of silver and ammonium parts with the whole of its sulphocyanide of silver by moderate dilution with water so completely in the form of a granular mass, that this plan may be employed in this case also as a method of separation in the analysis of this double salt. If, on the contrary, the solution prepared as above was mixed with caustic ammonia, it began slowly to become opalescent; single, nacreous, colourless laminæ began to separate, and the whole fluid was soon completely filled with these crystals, which, according to the analysis of Dr. Caldwell, proved to be sulphocyanide of silver. Muriatic acid acts in the same way, but the crystals soon break up into a granular powder. The process in this formation is certainly one of the most beautiful examples of a rapid formation of crystals, and in many respects reminds one of the mode of formation of thionurate of ammonia.

To ascertain positively whether this property is really to be ascribed to the double sulphocyanide of silver and ammonium alone, we prepared this double salt by the solution of a sufficient quantity of sulphocyanide of silver in sulphocyanide of ammonium. A moderately concentrated solution thus prepared, when mixed with aqueous ammonia, immediately showed the same phænomenon, as well as with muriatic acid; but the crystals obtained in the latter mode broke up very soon, and acquired the appearance of the sulphocyanide of silver obtained by simple dilution with water. The phænomenon is particularly remarkable when a fragment of the double compound, evaporated to dryness, is mixed with dilute ammonia in a watch-glass; the compound is then transitorily converted into an amorphous mass similar to chloride of silver, and a few moments afterwards the glass is filled with the most beautiful crystalline jelly. The potassium-salt behaves in the same way as the ammonium-salt.—Liebig's *Annalen*, October 1856, p. 76.

On the Action of Oxalic Acid upon Sugar.
By Dr. P. J. VAN KERKHOFF.

The author has studied the behaviour of oxalic acid towards sugar at high temperatures; he wished to ascertain whether oxalic acid

* Inaugural Dissertation, Göttingen, 1850.

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was decomposed by sugar, as by glycerine, into formic acid and water. The experiment has led to the preparation of a new humus-like substance.

About equal parts of a concentrated solution of loaf-sugar and ordinary crystallized oxalic acid, and in a second experiment equal parts of sugar-candy and oxalic acid, were heated in a retort. Water strongly impregnated with oxalic acid distilled over; the formation of formic acid and carbonic acid was but small, and the retort contained *a humus-like matter*, $C^{24}H^{10}O^{10}$, in the form of a brown or blackish-brown mass, which was but slightly attacked by potash even in boiling solution. Concentrated sulphuric acid acts but little upon it; with the assistance of heat it furnished sulphurous acid. Analysis gave—

C	63·05	24	61·54
H	4·52	10	4·27
O	..	10	34·19

The action of the oxalic acid in this case consists simply in a dehydratation of the sugar. (The formula of Maumené's *carameline* $=C^{12}H^{5}O^{5}$, comes pretty near this. The properties and mode of preparation lead to the supposition that the two bodies are identical. —*Knop.*)

The author adds, that this humus-substance approaches most closely to Mulder's *humine*, produced from sugar by strong mineral acids.—*Journ. für Prakt. Chem.*, lxix. p. 48.

Upon Æsculine. By Dr. F. Rochleder.

In conjunction with Dr. R. Schwarz, the author published several analyses of æsculine and æsculetine. Zwenger of Marburg also subsequently published an investigation of æsculine. The analyses of æsculetine made by Zwenger gave numbers exactly agreeing with the analyses of the author and Schwarz; on the other hand, Zwenger's analyses of æsculine differ essentially from those of the author.

When heated with dilute sulphuric acid, æsculine is decomposed into æsculetine and grape-sugar, and also by the action of muriatic acid. One weighed quantity of æsculine was decomposed by muriatic acid and another by sulphuric acid, and after the removal of the æsculetine the amount of sugar was determined by Fehling's method. 100 parts of æsculine furnished 52·09 to 52·70 parts of sugar ($=C^{12}H^{12}O^{12}$). This is the maximum obtained in the determinations. From this it follows with certainty that the formula of æsculine is $C^{60}H^{38}O^{37}$, and that of æsculetine $C^{18}H^{6}O^{8}$ or $C^{36}H^{12}O^{16}$.

If æsculine be boiled with baryta-water, in which it readily dissolves with a yellow colour, a similar decomposition takes place as by the action of acids, except that by boiling with baryta-water both the æsculetine and sugar undergo a further alteration.

Æsculetine takes up water, and becomes converted into æsculetic acid. The baryta-salt of this acid is constituted in accordance with

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the formula $C^{18}H^{11}O^{13}$, BaO; the lead-salt agrees with the formula $6(C^{18}H^{10}O^{12})+10PbO$. In its conversion into æsculetic acid therefore æsculetine takes up the elements of 4 equivs. of water, $C^{18}H^{6}O^{8}+4HO=C^{18}H^{10}O^{12}$ of supposed anhydrous acid. In this mode of decomposition the grape-sugar undergoes a conversion into glucic acid, and finally into apoglucic acid.

From grounds, which it would take too long to state here, it appears that æsculetine contains 1 equiv. of the radical of acetic aldehyde in place of 1 equiv. of hydrogen, and that its formula is $C^{14}\left\{\begin{matrix}C^{4}H^{3}\\H^{3}\end{matrix}\right\}O^{8}$, derived from $C^{14}H^{4}O^{8}$. In the shells of chestnuts there is an acid, and in the outer envelopes a nearly indifferent crystalline body, the composition of which first attracted attention with reference to this subject.—*Sitzungsber. der Akad. der Wiss. zu Wien*, xx. p. 351.

On Phoron. *By* Lies Bodart.

In 1849, in conjunction with Gerhardt, the author described an oil obtained by the dry distillation of camphorate of lime under the name of

Phoron, $C^{18}H^{14}O^{2}$, *i. e.* camphoric acid minus carbonic acid:—

$$C^{20}H^{14}O^{6}, 2CaO=C^{18}H^{14}O^{2}+2(CaO, CO^{2}).$$

The author has now found that phoron is also produced, together with Frémy's metacetone, by the dry distillation of grape-sugar with lime; its formation is expressed by the following equation:—

$$C^{24}H^{24}O^{24}=C^{18}H^{14}O^{2}+6(CO^{2})+10HO.$$

Treated with pentachloride of phosphorus, phoron furnishes

Perchloride of Phoryle, $C^{18}H^{13}Cl$, an oil which is lighter than water, of a very unpleasant smell, and boils at 347° F. This chloride, when sealed up in glass tubes with an alcoholic solution of ammonia, furnishes a crystalline body, which is probably the muriate of the corresponding azotized body, $C^{18}H^{5}N$, namely $C^{18}H^{5}N+HCl$.

By distillation with anhydrous phosphoric acid, a clear, strongly refractive oil, of an unpleasant odour, is obtained; it boils at 302° to 320° F. It is cumine, or an isomeric oil.

With potassium, phoron evolves hydrogen. The body thus produced is probably the compound $C^{18}H^{13}KO^{2}$.

Frémy's metacetone, which is produced by the dry distillation of sugar, is obtained when that portion of the oleaginous crude products of the distillation which passes at 187° F. is collected. The author indicates that this metacetone may probably have the formula $C^{18}H^{15}O^{3}$, instead of $C^{6}H^{5}O$. Its formation from sugar would then be easily explained:—

$$C^{24}H^{24}O^{24}=C^{18}H^{15}O^{3}+6(CO^{2})+9HO.$$

Comptes Rendus, xliii. p. 394.

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On the Action of Perchloride of Tin upon Starch at ordinary Temperatures. By H. von Payr.

At the inducement of Prof. Rochleder, who had observed that in microscopic sections of horse-chestnuts the starch disappeared after moistening with perchloride of tin, the author has endeavoured to investigate the change which is effected in starch by perchloride of tin at ordinary temperatures.

Starch, when mixed in a mortar with solution of perchloride of tin, dissolves, leaving a very small residue. The solution is poured away from the pasty residue and filtered, which takes place very slowly. The filtrate, when mixed with anhydrous alcohol, furnishes an abundant precipitate of a dazzling whiteness, which, when collected on a filter, was washed with anhydrous alcohol.

The salt was dried *in vacuo* over sulphuric acid, and gave on analysis—

C	23·41	23·20	60 =	360	23·43
H	4·11	4·16	64	64	4·16
O	33·81	33·97	64	512	33·36
SnO^2	38·67	38·50	8	599·344	39·04

If this tin-salt be triturated with water and a current of sulphuretted hydrogen gas passed into it, a limpid, colourless fluid is produced, which is filtered away from the yellow sulphuret of tin, and evaporated *in vacuo* over sulphuric acid, when it forms a white, amorphous, triturable mass of the following composition:—

C	40·90	24 = 144		41·02
H	6·67	23	23	6·55
O	52·43	23	184	52·43

When starch was treated with solution of perchloride of tin at 212° F., a paste was first produced, which afterwards dissolved; alcohol then precipitated a salt, exactly like the tin-salt above mentioned, and this, dried at 212° F., had the following composition:—

C	15·56	15·44	24 =	144	15·64
H	3·05	3·30	28	28	3·04
O	24·31	24·18	28	224	24·34
SnO^2	57·08	57·08	7	524·426	56·98

In the treatment of starch with solution of perchloride of tin with the aid of heat, the precipitate produced by alcohol in the solution scarcely amounts to the twelfth part of the quantity precipitated by alcohol from a solution of starch in perchloride of tin prepared in the cold.

The hydrate of carbon, $C^{24} H^{23} O^{23}$, which was separated from the salt prepared in the cold, is not a starch, for it readily dissolves in water, and is not coloured blue by iodine. It is neither a dextrine nor a sugar, but is easily converted into sugar by being heated with dilute mineral acids. From its properties and composition, it holds an intermediate position between sugar and dextrine:—

$$C^{24} H^{23} O^{23} = C^{12} H^{12} O^{12} + C^{12} H^{11} O^{11}.$$

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It is produced, like sugar, from starch, by taking up the elements of water; but its formation takes place very rapidly, almost instantaneously, and without any evolution of heat. It is an indifferent body, so that its salts are difficult to obtain of a constant composition, and are of no decisive value in the determination of the atomic weight.—*Sitzungsber. der Akad. der Wiss. zu Wien*, xxi.

On the Preparation of Hydrate of Baryta. By Dr. Mohr.

For the preparation of hydrate of baryta, sulphuret of barium is treated with oxide of copper, or nitrate of baryta is calcined.

The author states that it is obtained more easily, and without calcination, by boiling caustic soda with the corresponding quantity of nitrate of baryta, filtering it whilst hot, and leaving it to crystallize. A weak solution of caustic soda is prepared from pure carbonate of soda and caustic lime in the usual way, and evaporated in a cast-iron vessel until its specific gravity is 1·10 to 1·15. To ascertain the exact quantity necessary for the decomposition, 10 cub. centims. of a normal solution of oxalic acid (63 grms. acid in the litre) are taken up in a pipette, a few drops of tincture of litmus are added to it, and the solution of soda is then added from a graduated pipette until the tincture of litmus becomes blue. The number of cubic centimetres of soda is then read off, and multiplied by one hundred; to the number of cubic centimetres of solution of soda thus obtained, 1 atom or 130·5 grms. of nitrate of baryta are taken.

Supposing 4·5 cub. centims. of solution of soda have been employed for 10 cub. centims. of solution of oxalic acid, 130·5 grms. of nitrate of baryta are taken for 450 cub. centims of solution of soda. This lies in the system of the volumetric method, that 1 atom of substance is taken to 1 litre of fluid for compounds in equal atomic weights. In the absence of pipettes and litre-bottles, we may proceed in the following manner:—

Weigh off exactly 63 grs. of pure oxalic acid (or 75 grs. of pure tartaric acid), dissolve them in water, add a little tincture of litmus, and then pour in solution of soda from a weighed bottle filled therewith until the tincture of litmus becomes blue. The quantity of solution of soda employed is then weighed, and this takes 130·5 grs. of nitrate of baryta.

After the proportion is ascertained, the nitrate of baryta is triturated to powder, the solution of soda boiled up in a flask, and the nitrate of baryta added to it, the boiling being continued. A slight precipitate is produced, in consequence of a retention of carbonic acid in the soda, and possibly also from sulphate of baryta, if the solution of soda were not quite free from sulphuric acid. After everything is dissolved by boiling, for which purpose small quantities of distilled water are added, it is filtered as quickly as possible, and whilst hot, through a folded filter with a covered funnel, into another flask, and allowed to cool slowly in the cellar, the flask being placed in a basket with straw, or otherwise protected from being cooled too rapidly. In a minute or two we find an abundant crystallization,

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and sometimes, according to the concentration of the solution of soda, a solidified mass of crystals of baryta. By shaking, some mother-liquor always separates. The crystals are put upon a funnel stopped with a plug of cotton, and allowed to drain, shaking the funnel occasionally, until nothing more runs off. Afterwards the filter is put upon a centrifugal machine, by means of which large quantities of fluid flow away from crystals which have been drained for days. The crystals of baryta are obtained as a still moist mass of large plates, and may be employed in this state for most purposes. If a residue of nitric acid be injurious, they may be recrystallized. In all decompositions in which the hydrate of baryta is calcined, a small residue of nitric acid is of no consequence, as also in absorptions of carbonic acid.

Chloride of barium may also be employed, and also caustic potash with baryta-salts. But traces of chlorine are generally far more injurious than those of nitric acid, because determinations of chlorine occur in so many analyses; and solution of potash is far less easy to prepare pure than solution of soda. The fluid which flows from the crystals of baryta is always a saturated baryta-water, and may be employed in determinations of carbonic acid. In the moist state the product amounts to something more than the equivalent. On the large scale, the boiling may be effected in a covered cast-iron kettle; and it may be allowed to settle without boiling and drawn off by a siphon, as in the preparation of caustic potash.—*Archiv der Pharm.*, lxxxviii. p. 38.

On a new Cinchona Bark and its Alkaloid, Cinchonidine.
By M. Wittstein.

The author has obtained from M. Geith, of the firm of Ammon and Geith of Nuremberg, a new Cinchona bark, which was forwarded to him from Hamburg as *Cortex Chinæ rubiginosus*. Its mode of packing was exactly like that of the *C. Calisaya*. Of its origin nothing further could be ascertained than that the bark was obtained from London, and the name was only attached to it in Hamburg.

From an exact examination, and a determination effected by Prof. Mettenheimer of Giessen, it appeared to belong to the genus of barks known under the names of *Cinchona flava*, *Carthagena*, *aurantiaca*, and *C. flava fibrosa*, which are not rich in alkali.

According to the investigation made of this bark by the author, it has much resemblance to the *Cinchona regia* or *Calisaya*, but differs greatly therefrom in its chemical composition. The author therefore calls it

Cinchona pseudo-regia.—It forms strong, smooth fragments, without epidermis, and with a fibrous fracture; its taste is bitter, and its colour is between that of *C. regia* and *C. rubra*. In the cold extract of 20 grs. of bark,—

Tartrate of potash produces a gray turbidity;

Tannic acid, a gray precipitate;

Perchloride of iron, a greenish-yellow colour with a slight turbidity;

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Oxalate of ammonia, a slight white turbidity;
Ammonia, a reddish-gray turbidity; and
Acetate of lead, a whitish turbidity, from which a reddish-gray precipitate gradually settles.

This bark contains a new alkaloid, which the author calls *Cinchonidine*, $C^{18} H^{10} NO$.—It crystallizes in colourless, shining needles and prisms, 1 to 2 lines in length, belonging to the oblique rhombic system. It is inodorous and bitter. The cold, saturated, alcoholic solution has a distinct alkaline reaction; the ætherial solution has a very weak alkaline reaction, and the aqueous solution produces no change on vegetable colours. The alcoholic solution tastes extremely bitter, almost like quassia; the ætherial and aqueous solutions of course taste less bitter in proportion to their smaller amount of alkaloid. On platinum foil it fuses into a colourless liquid, which evolves fumes smelling not unpleasantly like oil of bitter almonds; at the same time it becomes brown, ignites, and burns with a smoky flame, without leaving a trace of residue. By trituration it furnishes a snow-white electrical powder. The alkaloid loses nothing in weight up to 212° F., and even to its melting-point of 336° to 338° F. Its solubility is as follows:—

1	part dissolves in	398	parts of æther of sp. gr. 0·740 at 61°–68° F.
1	...	88	parts of alcohol of sp. gr. 0·833 at 61°–68° F.
1	...	19	parts of alcohol of sp. gr. 0·833 at boiling heat.
1	...	3287	parts of water at 61°–68° F.
1	...	596	parts of water at boiling heat.

The new alkaloid behaves as follows towards reagents:—

Freshly prepared chlorine-water dissolves it readily without colour; liquid ammonia, gradually dropped into this solution, produces at first a light, flocculent, grayish-white precipitate, which floats upon the dingy yellow fluid, but disappears with the greatest facility by the addition of an excess of ammonia, whilst the fluid again appears clear wine-yellow. Concentrated sulphuric acid dissolves it rapidly; the solution is colourless, and undergoes no perceptible alteration by being gently heated. Concentrated nitric acid and concentrated muriatic acid behave in the same way. It also dissolves with the greatest facility in dilute acids, and saturates them completely. The solution in muriatic acid was prepared by adding the powdered alkaloid to 1 oz. of hot water acidified by the addition of 5 drops of muriatic acid of spec. grav. 1·13 until the last portion did not disappear. It did not alter either litmus- or turmeric-paper, and behaved towards some reagents in the following manner:—

Caustic alkalies produced white, densely flocculent precipitates, which rapidly acquired a granular crystalline appearance. Alkaline carbonates behaved in the same way; these precipitates dissolved quietly in acids after washing, so that they were free from carbonic acid. Phosphate of soda also gave a white, densely flocculent precipitate, which quickly became granular crystalline. Perchloride of mercury gave a strong white turbidity, which remained finely flocculent. Perchloride of gold gave a yellow turbidity, which rapidly

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caked together into pale citron-yellow flakes. Perchloride of platinum furnished a pale orange-yellow, finely flocculent precipitate, which underwent no further change. Protonitrate of palladium gave a pale orange-yellow, finely flocculent precipitate, which also retained its original nature. Sulphocyanide of potassium produced a white turbidity, which quickly united into a granular crystalline form, and adhered firmly on the walls of the vessel. Iodide of potassium the same, except that the transition to the granular crystalline form took place more slowly. Biniodide of potassium gave a strong brownish-yellow precipitate united into thick flakes. Tannic acid, a milk-white, finely flocculent precipitate, which underwent no further change in its appearance.

By distillation with potash, the alkaloid appears to furnish chinoline. Analysis:—

C	77·863	77·272	18 =	1350	77·143
H	7·185	7·296	10	125	7·143
N	9·896	..	1	175	10·000
O	..	..	1	100	5·714

The *platinochloride* is a pale orange-coloured precipitate, tolerably hygroscopic. It contained 28·47 and 28·49 per cent. of platinum (calculated, 28·495). This alkaloid is homologous with cinchonine, $C^{20}H^{12}NO$, cinchonine—$C^{2}H^{2} = C^{18}H^{10}NO$, cinchonidine.

In the investigation of the bark, &c., T. Crawford and H. Krombach took part. The following analysis of the ashes of the new bark was made by the latter chemist. The ashes consist for the most part of carbonate of lime.

1000 grs. of air-dried powdered bark lost 75 grs. by drying at 212° F. The remaining 925 grs. furnished 19·98 grs. of tolerably white ashes. The amount of ash in the air-dried bark therefore is 1·996 per cent., and in the bark dried at 212° F. 2·157 per cent. The composition of the ashes was—

Potash.....	5·32	Chlorine.....	2·23
Soda	5·82	Sulphuric acid ..	3·62
Lime	38·78	Phosphoric acid..	3·32
Magnesia	0·50	Silica.....	6·88
Alumina.....	1·00	Carbonic acid ..	32·33
Oxide of iron....	0·80		

Wittstein's *Vierteljahrschrift*, v. p. 311.

On the Fats of the Bile, *By* M. Gobley.

The author has ascertained by experiment that the oleic and margaric acids of the bile do not pre-exist in it, as is usually supposed; they are products of the decomposition of lecithine, which is decomposed by chemical reagents and by putrefaction. Olein and margarine, cholestearine, and especially lecithine, must be reckoned amongst the fats of the bile. The fats of the bile, when they reach the intestine, must be taken up by it. Only traces of olein, margarine, and cholestearine are found in the excrements. We may not

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conclude that the bile is of no use in the nutritive process, and merely a mass thrown off by the organism; for as its fats are almost entirely taken up by the intestinal canal, an animal deprived of its bile must take more nutriment to replace this.—*Journ. de Pharm. et de Chim.*, 3 sér. xxx. p. 241.

On the so-called Phosphatic Acid. By M. Pagels.

It is still generally supposed, with Dulong, that the acid produced by the slow combustion of phosphorus in the air is a definite compound of phosphorous and phosphoric acids, which has been called *phosphatic acid* by Pelletier. We find no satisfactory information anywhere as to how the proportions between PO^3 and PO^5 have been determined. The author has investigated this acid in Mitscherlich's laboratory, and employed solution of perchloride of mercury as a means of determination for phosphorous acid. Phosphorous acid separates protochloride of mercury therefrom.

The experiments showed that the phosphatic acid is not a definite compound, but a mixture of variable proportions of PO^3 and PO^5. The author indicates that the phosphoric acid prepared with nitric acid and phosphorus for internal administration should be tested with perchloride of mercury for phosphorous acid, as the latter is poisonous.—*Journ. für Prakt. Chem.*, lxix. p. 24.

ANALYTICAL CHEMISTRY.

On the Detection of the Poisonous Alkaloids. By F. I. Otto.

The author refers to the method of Stass for the detection of organic bases in cases of poisoning (see Chem. Gaz. vol. x. p. 348), which has now taken the place of all the older methods. In this the alkaloids are dissolved by æther, which is selected in preference to alcohol, because it has much less solvent power upon the substances present with the alkaloids, when the fats are first of all got rid of. The insolubility of the salts of the alkaloids in æther also enables them to be freed from the matters which are soluble in æther, and which prevent their crystallization or preparation in the pure state, and disturb the reactions.

Stass has only prescribed the treatment of the alkaloids, as sulphates with æther, in the case of the volatile alkaloids. He agitates the ætherial extract of the impure alkaloid with water to which a fifth of sulphuric acid is added, pours away the æther which takes up animal substances, washes the aqueous solution of the acid salt of the alkaloid repeatedly with æther, then decomposes it with caustic potash or soda, and so transfers the purified alkaloid to æther.

The author proposes to extend this process to the non-volatile alkaloids. The operation may be exactly the same as with the volatile alkaloids, namely, agitation of the ætherial solution with water acidulated with sulphuric acid, &c.; or the solution may be allowed

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to evaporate spontaneously, the remaining impure alkaloid dissolved in a little water containing sulphuric acid, and this solution repeatedly agitated with æther. If carbonate of soda be then added in excess and the alkaloid taken up by æther, the ætherial solution leaves it in a very pure state, and for the most part crystalline by evaporation. The author considers the latter method as the most advisable with the non-volatile alkaloids, as these are generally less soluble in æther than the volatile alkaloids.

Even if the æther took up a trace of salt from the solution of the alkaloid, it would still be advisable to let this be lost in order to obtain a purer alkaloid, for it is far better to have a small quantity in a pure state than a larger quantity impure. Thus, for example, in operating upon food containing strychnine according to the process of Stass, if an ætherial solution of the alkaloid has been obtained, and a drop of concentrated sulphuric acid be let fall upon the residue of the evaporation of this solution, the brownish coloration produced shows at once that the reaction with chromate of potash will not come out in all its beauty. If a little water be then added and the purification carried out as above described, crystalline scales of the alkaloid are found in the residue of the evaporation of the ætherial solution then formed, and of these every perceptible particle is sufficient to give the reaction with sulphuric acid and chromate of potash with the greatest beauty.

The treatment of the alkaloids as salts with æther may, however, be carried out by the process of Stass, before their transference to æther. This is the mode adopted in his laboratory. Food containing strychnine, for example, is digested with strong alcohol with the addition of oxalic or tartaric acid, and filtered; the extract is evaporated, the watery fluid, if necessary with an addition of some water, is filtered from the fat, resin, &c., and again evaporated, the residue extracted with absolute alcohol, evaporated, and again taken up by a little water. Instead of setting free the alkaloid at once from this solution by alkali and transferring it to æther, the solution is first repeatedly agitated with æther as long as the latter becomes coloured and leaves a residue on evaporation, and then carbonate of soda is added and the alkaloid dissolved in æther. It will remain in a very pure state on the evaporation of this solution.

Detection of Morphine.—During repeated operations according to the method of Stass in the author's laboratory, morphine could not be detected with any certainty. This was due to the extremely small solubility of morphine in æther and the solubility of the alkaloid in solution of soda. The latter was shown by the fact that more morphine could be transferred to æther when an alkaline carbonate was employed for its separation instead of caustic alkali. For this reason the author advised (in the first edition of his 'Anleitung') that the alkaline fluid, repeatedly treated with æther, should not be thrown away, but mixed, after evaporating the æther and adding some solution of soda, with a concentrated solution of muriate of ammonia, and left standing in an open vessel. Crystals of morphine are then obtained, if morphine be present. He subsequently learnt

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from Polstorf, that he had been able to detect morphine by the process of Stass, and Von Pöllnitz also showed him crystals of morphine which remained after the evaporation of the æther.

Von Pöllnitz found that the solution of a salt of morphine, when mixed with carbonate of soda and then immediately agitated with æther, gives up morphine to the latter, and this crystallizes on the evaporation of the solution. But if the morphine have time to crystallize before the agitation with æther, the æther scarcely takes up any of it. To transfer morphine to æther, therefore, the solution of the salt of morphine mixed with bicarbonate of soda must be agitated with æther immediately after the addition of the soda-salt, and the ætherial solution obtained poured away as soon as possible and allowed to evaporate.

Polstorf found that æther containing alcohol dissolved a larger quantity of morphine than pure æther.

Testing of the Alkaloids.—After the evaporation of the ætherial solution of the non-volatile alkaloids, finally in a warm place, there often remains in the upper part of the dish a ring of yellow, amorphous, impure alkaloid, but below this pure alkaloid, more or less distinctly crystallized. Narcotine, obtained when opium is present, occurs in the largest crystals. Strychnine forms small, isolated crystals similar to morphine. Veratrine appears pulverulent or resinous; colchicine could only be obtained in a resinous form.

For testing, single particles are removed with the point of a penknife. Testing with the reagents which produce a characteristic colour is best performed in a small porcelain dish, the whiteness of which shows the colour most distinctly. Testing with the reagents which produce colourless or nearly colourless precipitates is best performed in small watch-glasses, placed upon a dark surface to render the precipitates as perceptible as possible.

In general only the presence of one or other of the alkaloids has to be detected. But if there be no indications of the nature of the alkaloid, it must be tried. In what sequence the trials are made is of little consequence. A particle is put into a drop or two of sulphuric acid in a porcelain dish and warmed; a red colour indicates veratrine. A particle is dissolved in concentrated sulphuric acid, and tested with chromate of potash for strychnine. In a few drops of solution of iodic acid, a yellow colour and odour of iodine indicate morphine; the addition of a little potato-starch paste then produces blue iodized starch. The solution of a particle in water with a trace of muriatic acid, and addition of dilute neutral solution of perchloride of iron by means of a glass rod, gives the blue colour indicative of morphine. A particle is mixed with a few drops of concentrated nitric acid; a violet colour indicates colchicine. Brucine (from *nux vomica*) colours moderately concentrated nitric acid red; the addition of solution of protochloride of tin with a glass rod produces a beautiful blue or violet colour. Concentrated sulphuric acid with a trace of nitric acid, when heated with narcotine, acquires a dark red colour. Narcotine is also well characterized by its insolubility in water containing acetic acid.

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When the alkaloid has been recognized, the other reactions are tried with the residue in the dish; it is dissolved in water with a trace of sulphuric or muriatic acid, and this solution is tested with tannin, perchloride of gold, perchloride of platinum, sulphocyanide of potassium, &c.

The volatile alkaloids coniine and nicotine are recognized by their fluid state and odour. The penetrating, repulsive odour of coniine distinguishes this alkaloid from nicotine, which is also pretty soluble in water, whilst coniine is but slightly soluble. The odour of both alkaloids disappears on neutralization with an acid, such as oxalic acid; caustic potash reproduces it.

In the author's laboratory, the red chromate of potash was always preferred as a reagent for strychnine. It is necessary to take a quantity of the chromate corresponding with that of the alkaloid in order to make sure of the reaction, and this is best obtained with a fragment of the salt than with the powdered salt or a solution. When the alkaloid is dissolved in sulphuric acid in a porcelain saucer, and the solution has become diffused over the saucer, a fragment of chromate of potash is put in. By inclining the saucer, violet streaks then run down from the salt; and if the latter be pushed about with a glass rod, the whole fluid is soon of a beautiful violet. A single drop of the ætherial solution leaves so much of the alkaloid, that it may be recognized in this way with the greatest certainty by means of a drop of sulphuric acid and a particle of chromate of potash. The author mentions a case in which the alkaloid was not detected with certainty because it was in considerable quantity, and too small a quantity of powdered chromate of potash was stirred into it. By the use of a fragment of the salt, the reaction must always make its appearance distinctly round it at some time; when the reaction is produced, the fragment is pushed to other places, in order that it may not be destroyed by an excess of the salt. If much alkaloid be found, the chromate of potash is crushed with a glass rod, and by stirring it a beautiful blue mass is obtained.

During Palmer's trial it was stated in the papers that strychnine could not be detected in the presence of antimony. Every one who understood the subject knew that this was incorrect. The fact was afterwards explained by Von Sicherer. The tartrate of antimony, the best known of all the salts of antimony, prevents the reaction by which strychnine is recognized, in consequence of its containing tartaric acid, not antimony, this acid acting in this case like any other powerfully deoxidizing substance. To get rid of the tartaric acid, Von Sicherer recommended its destruction by means of concentrated sulphuric acid; the strychnine is then to be extracted by chloroform after the supersaturation of the mass with carbonate of soda. The author regards the use of sulphuric acid as very doubtful. In practiced hands it may give a good result, but otherwise strychnine will also be destroyed by it. The whole process of decomposition is superfluous. If the substances containing strychnine be treated by the process of Stass, no tartrate can occur with the strychnine separated. He has dissolved strychnine in water con-

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taining tartaric acid, mixed an excess of carbonate of soda with the solution, and agitated the mass with æther. The ætherial solution gave such pure strychnine, that the reaction was obtained therewith in great purity.

Morphine cannot be detected with perchloride of iron by any means so certainly as strychnine with sulphuric acid and chromate of potash. The best solvent for morphine is muriatic acid, of which however any excess must be avoided as much as possible. If the solution of morphine be very pure and the proper quantity of chloride of iron be used, a very beautiful blue colour is obtained. A glass rod is dipped into the iron solution, and then put into the solution of morphine. If the morphine be less pure, or the solution be only in slight excess, the colour is greenish.

If a few drops of concentrated sulphuric acid be poured over morphine in a dish, heated until the solution of the alkaloid, and then diluted with a little water, a particle of chromate of potash produces an intense mahogany-brown colour in the fluid.—Liebig's *Annalen*, October 1856, p. 39.

Assay of the Acids of Commerce. *By* M. Violette.

The author proposes to employ Gay-Lussac's alkalimeter in the assay of the acids of commerce; all that is necessary is to add to the reagents of the alkalimeter a solution of saccharate of lime, and to operate with the same utensils and in the same way as with the assay of potashes. The principle of the process is as follows:—If we saturate by the quantities b and b' of the same base, the quantities a and a' of two different acids of which the equivalents are e and e', we have

$$\frac{a}{a'} = \frac{e}{e'} \times \frac{b}{b'}.$$

If for a we take 1 grm. of the acid to be assayed, for a' 1 grm. of normal sulphuric acid of which the density is $e=612{\cdot}50$, and such as is indicated by Gay-Lussac in the assay of potashes, and if we denominate T the centesimal strength of the acid a, or the quantity of real acid contained in 100 parts, we get the general formula

$$T = 100 \times \frac{e}{612{\cdot}50} \times \frac{b}{b'} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The values b and b' will be determined by the quantities of saccharate of lime necessary to saturate the acids and given by experiment; as to the value of e, it will be found in the chemical tables. By substituting this in the formula (1) for each acid, we get the following formulæ, giving each acid its centesimal strength.

Sulphuric acid:—

$$T = 100 \times \frac{612{\cdot}50}{612{\cdot}50} \times \frac{b}{b'} = 100 \times \frac{b}{b'} \quad . \quad . \quad . \quad . \quad (2)$$

Muriatic acid:—

$$T = 100 \times \frac{455{\cdot}70}{612{\cdot}50} \times \frac{b}{b'} = 74{\cdot}40 \times \frac{b}{b'} \quad . \quad . \quad . \quad (3)$$

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Nitric acid:—

$$T = 100 \times \frac{787{\cdot}50}{612{\cdot}50} \times \frac{b}{b'} = 128{\cdot}57 \times \frac{b}{b'} \quad . \quad . \quad . \quad (4)$$

Acetic acid:—

$$T = 100 \times \frac{750}{612{\cdot}50} \times \frac{b}{b'} = 122{\cdot}44 \times \frac{b}{b'} \quad . \quad . \quad . \quad (5)$$

As an example of the mode of proceeding, let an ordinary commercial muriatic acid of density 1·16 be assayed.

First Operation.—Weigh off 50 grms. of the acid, dilute them with water to ½ a litre; take 50 cub. centims. of this solution (representing 1 grm. of acid) with a pipette, redden them with a few drops of tincture of litmus, and drop into it a solution of saccharate of lime by means of an alkalimetric burette, until the change of the colour to blue indicates that the saturation is complete; the number b of divisions of the burette employed is 24.

Second Operation.—With the pipette take 50 cub. centims. of a *normal* sulphuric acid (containing 1 grm. of hydrated sulphuric acid), redden them with litmus, and saturate them with saccharate of lime in the same way as above; the number b' of divisions of the burette employed is 53.

By substituting the values b and b' in the formula (3), we have

$$T = 74{\cdot}40 \times \frac{24}{53} = 33{\cdot}83 \text{ per cent.}$$

In the tables arranged by Davy, we find that muriatic acid, of which the density is 1·17, contains 34·34 per cent. of actual acid. This approximation gives confidence in the process.

The preparation of the reagents is indicated by Gay-Lussac in his assay of potashes; the saccharate of lime is prepared by digesting in the cold 50 grms. of caustic and slaked lime in a litre of water containing 100 grms. of sugar.—*Comptes Rendus*, Nov. 24, 1856, p. 1010.

On the Indirect Determination of Iron by Sulphuretted Hydrogen. By Prof. Delffs.

The author has had some experiments made with a view of determining iron from the quantity of sulphur which is precipitated when salts of peroxide of iron are reduced to protoxide by sulphuretted hydrogen. The sulphur is united by exposure to heat, by which it cakes together, and then weighed in substance. The double sulphate of iron and ammonia was employed in the experiments; the amount of peroxide of iron in this was calculated according to the formula $Fe^2O^3, NH^4O, 4SO^3 + 24HO$. The experiments are as follows:—

First Experiment.

Quantity of iron-alum = 6·7653 grms.

Quantity of sulphur found	= 0·2257
Quantity of sulphur calculated.....	0·2245
Difference.....	= +0·0012

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Second Experiment.

Quantity of iron-alum=3·6702.

Quantity of sulphur found	=0·119
Quantity of sulphur calculated.....	0·119
Difference	0·000

Third Experiment.

Quantity of iron-alum=7·0512.

Quantity of sulphur found	=0·2345
Quantity of sulphur calculated.....	0·2340
Difference.....	=+0·0005

Fourth Experiment.

Quantity of iron-alum=1·011.

Quantity of sulphur found	=0·0335
Quantity of sulphur calculated	0·0330
Difference.....	=+0·0005

From this it appears that iron may be determined by sulphuretted hydrogen, and that the quantities of sulphur thrown down during the reduction correspond with a decomposition in accordance with the equation

$$Fe^3O^3 + HS = 2FeO + HO + S.$$

The method may be of especial service in some analyses, particularly in those in which peroxide of iron has to be determined in the presence of protoxide.—*Neues Jahrbuch für Pharm.*, vi. p. 1.

Volumetric Process for the Detection of the Adulteration of Potashes with common Salt. *By* F. Muck.

All potashes contain common salt, but normally no more than that the amount of chlorine may be 2 per cent. If the maximum normal amount of chlorine be taken at 2·5 per cent. for dry potash, the excess appears as an intentional addition. The author therefore prepares a normal silver solution for the examination of potash for its amount of common salt; this contains $4\frac{1}{2}$ grs. of fused nitrate of silver in 100 cub. centims. A cubic centimetre of this fluid indicates exactly $\frac{1}{100}$ gr. of chlorine.

Of the potash to be tested, 10 grs. are supersaturated with nitric acid, and mixed with 25 cub. centims. of the silver solution. The chloride of silver is allowed to settle, and then a few drops more of the silver solution are added. If no precipitate is thus produced, the potash is not intentionally adulterated with salt, for as the silver solution corresponds with $\frac{1}{4}$ gr. of chlorine in 10 grs. of potash, the latter contains at the utmost 2·5 per cent. of chlorine.—Wittstein's *Vierteljahrsschrift*, v. p. 538.

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THE CHEMICAL GAZETTE.

No. CCCXLIII.—February 1, 1857.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Cobaltate of Potash. *By* Prof. L. PEBAL.

AT the recommendation of Bunsen, the author has investigated the cobaltate of potash described by Schwarzenberg*. Schwarzenberg determined the amount of oxygen in cobaltic acid only from the loss. To establish the existence of this acid, the author has made the following experiments.

The amount of oxygen may be easily ascertained by Bunsen's volumetric method, as the compound is completely dissolved in strong, hot muriatic acid, with formation of protochloride of cobalt and evolution of chlorine.

The quantity of iodine in one degree of the burette of the solution of iodine to be employed in the estimation of the oxygen, was first determined with chromate of potash by the following experiments:—

First Preparation.—The aqueous solution of the residue of fusion was rendered turbid by light, brown flakes. These were carefully removed by lixiviation with water. Shining and comparatively large crystals.

First Experiment.—Substance dried over sulphuric acid.

$$A=0{\cdot}3203;\ n=5;\ t=19{\cdot}2;\ t^{1}=1{\cdot}7.$$

Calculated according to the formula

$$x=\frac{100\,.\,O\,.\,a}{A\,.\,I}(nt-t^{1}),$$

the per-centage amount of separable oxygen is

$$x=10{\cdot}24.$$

The substance also gave 0·0081 grm., representing 2·53 per cent. of silver.

Second Experiment.—Dried at 212° F.

$$A=0{\cdot}3122;\ n=5;\ t=22{\cdot}8;\ t^{1}=21.$$
$$x=10{\cdot}35.$$

Third Experiment.—Dried at 212° F.

$$A=0{\cdot}3055;\ n=5;\ t=21{\cdot}6;\ t^{1}=15{\cdot}1.$$
$$x=10{\cdot}58.$$

* See Chem. Gaz., No. 324, April 15, 1856.

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Fourth Experiment.—Dried at 212° F.

$$A=0{\cdot}3006\,;\ n=5\,;\ t=21{\cdot}7\,;\ t^{1}=19{\cdot}1.$$
$$x=10{\cdot}35.$$

For the determination of the cobalt, the solution poured out of the volumetric flask was evaporated to dryness on the water-bath, the residue diluted with water, the chloride of silver separated by filtration, and the filtrate precipitated whilst boiling in a platinum dish with pure potash. The precipitate was carefully washed by decantation, and strongly calcined. As the composition of the protoperoxide of cobalt varies according to the degree and duration of the calcination, the corresponding quantity of protoxide of cobalt was determined volumetrically.

The quantity of the calcined protoperoxide of cobalt was 0·2312 grm. Of this, 0·2097 grm. was employed in fine powder for determination.

$$A=0{\cdot}2097\,;\ n=3\,;\ t=20{\cdot}4\,;\ t^{1}=19{\cdot}9.$$

From these numbers, calculated for the quantity 0·2312 grm., there was an amount of oxygen of 0·0158 grm. contained in the protoperoxide of cobalt more than corresponds with the composition of the protoxide.

If we deduct this 0·0158 grm. of oxygen from the 0·2312 grm. of protoperoxide of cobalt, we get 0·2154 grm., or calculated for 100 parts of cobaltate of potash, 71·62 per cent. of protoxide of cobalt, which, with the amount of oxygen found by the volumetric method (10·35 per cent.), compose anhydrous cobaltic acid.

Fifth Experiment.—Dried at 212° F.

$$A=0{\cdot}3043\,;\ n=6\,;\ t=17{\cdot}9\,;\ t^{1}=14{\cdot}0.$$
$$x=10{\cdot}68.$$

The further analysis gave 0·0095 of chloride of silver, representing 2·33 per cent. of silver and 0·2344 grm. of protoperoxide of cobalt. The volumetric determination of the latter gave the following numbers:—

$$A=0{\cdot}2266\,;\ n=3\,;\ t=20{\cdot}7\,;\ t^{1}=17{\cdot}6.$$

From this we find the quantity of protoxide of cobalt,—

$$0{\cdot}2344-0{\cdot}0160=0{\cdot}2184,\text{ or }71{\cdot}77\text{ per cent.}$$

Sixth Experiment.—Dried at 212° F.

$$A=0{\cdot}3276\,;\ n=5\,;\ t=23{\cdot}1\,;\ t^{1}=14{\cdot}2.$$
$$x=10{\cdot}76.$$

Chloride of silver, 0·0095 grm., representing 2·17 pe
of potash, 0·0875 grm.; in 100 parts, 14·44 per

Seventh Experiment.—From 0·3098 grm.
212° F., there were obtained 0·0834 gr
representing 14·99 per cent. of potash
phate of cobalt, representing 71·99 r

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The results of the separate analyses are therefore as follows:—

	O.	CoO.	KO.	Ag.
1.	10·24	..	..	2·53
2.	10·35			
3.	10·58			
4.	10·35	71·62		
5.	10·68	71·77	..	2·33
6.	10·76	..	14·44	2·17
7.	..	71·99	14·99	
Mean	10·52	71·79	14·71	2·34

Whether we regard the silver intermixed as oxide or metallic silver, we must in the calculation adopt the quantity of oxygen equivalent thereto in the composition of the entire substance, because in the latter case the equivalent quantity of chlorine remained combined with silver in the volumetric determination.

From this we get the following per-centage composition:—

CoO	71·79	Ag	2·34
O	10·52	O	0·17
KO	14·71		
			99·53

The conditions under which the compound is produced render an intermixture of oxide of silver very improbable. The amount of oxygen equivalent to the silver must therefore be added to that found by the volumetric method.

If we select protoxide of cobalt as the starting-point, we get the following equivalent proportions:—

Protoxide of cobalt.		Oxygen.
3	:	2·09
		Potash.
6	:	0·98

or 3 equivs. cobalt to 5 equiv. oxygen,
and 6 equivs. cobalt to 1 equiv. potash.

If with 6 equivs. of cobalt the compound contained only 1 equiv. of water, its quantity must amount to nearly 3 per cent. The sum of the constituents found, however, alone reaches 99·53 per cent. Taking into consideration the very slightly discordant analytical data, it is therefore very improbable that this compound contained water belonging to its constitution.

If we eliminate the accidental amount of silver, and calculate the other constituents for 100 parts, we get the following composition:—

Protoxide of cobalt.....	73·87
Oxygen	10·99
Potash.....	15·14

The formula $Co^6 O^{10} KO$ requires—

6CoO	2811·6	73·99
O^4	400·0	10·53
KO	588·9	15·48

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Second Preparation.—The smaller laminæ only contained traces of silver.

A=0·3171 (dried at 212° F.); n=5; t=23·2; t^1=18·5.
x=1069.

In the above substance, 0·4823 grm. of protosulphate of cobalt were found.

The compound therefore contained 73·53 per cent. CoO, 10·69 per cent. O.

These numbers correspond with the atomic proportion,—

3 : 2·4 or Co^3 : O^5.

These experiments consequently lead undoubtedly to the composition given by Schwarzenberg.

Third Preparation.—The crystals obtained by long-continued fusion were very small.

0·5438 grm., dried at 212° F., gave—
0·8323 grm. protosulphate of cobalt,
0·1123 grm. sulphate of potash,
0·0124 grm. chloride of silver.

0·3320 grm., dried at 212°, only lost 0·0008 grm. in weight by heating to 392° F. for several hours.

0·2252 grm., dried at 212° F., lost 0·0145 grm. by strong calcination.

Calculated for 100 parts:—

Protoxide of cobalt.....	74·06
Potash.....	11·19
Silver	1·71
Loss by calcination.....	6·44

The volumetric determination of the calcined substance gave the following numbers:—

A=0·1985; n=2; t=23·7; t^1=12·4.
x=6·14.

By the volumetric treatment of the uncalcined substance, 9·66 per cent. of oxygen were found. But this number can only be taken as a minimum, because some chlorine escaped in consequence of an imperfect closure of the caoutchouc. We are justified in supposing that in this compound also the atomic proportion was Co^3 O^5, and that consequently, instead of 9·66, about 10·5 per cent. ought to have been found.

The amount of oxygen in the calcined material (6·14 per cent.) represents 5·74 per cent. in the uncalcined compound, and the difference,

10·5—5·74=4·76,

expresses the maximum amount of oxygen evolved during calcination.

If the amount of protoxide of cobalt in the calcined substance be calculated from the above analysis, it amounts to 79·16. From this, and the amount of oxygen determined by the volumetric process

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(6·14), the atomic proportion of the protoxide of cobalt to the oxygen is as=3 : 1·09. The residue of calcination therefore contains, besides potash, which is extractible by water, protoperoxide of cobalt, $Co^3 O^4$.

As the behaviour of the substance at 392° F. differs from that observed by Schwarzenberg, the author repeated the experiment with a mixture derived from several preparations.

0·8120 grm. of this, dried at 212° F., lost 0·0017 grm. by being exposed to a heat of 392° F. for several hours. This loss of weight is so small, that it may properly be attributed to errors of observation. The loss by calcination was 4·95 per cent.

The correct determination of the oxygen testifies to the excellence of Schwarzenberg's analysis. If the author's results with regard to the amounts of water, potash, and the stability of the compound at 392° F. exhibit a difference, this appears to depend upon the production of different compounds, in consequence of variations of temperature and of the duration of the fusion.—*Sitzungsber. der Akad. der Wiss. zu Wien*, xxi. p. 169.

Triphenylamine, a Product of the Decomposition of the Bisulphite of the Ammoniacal Cinnamic Aldehyde. By A. Gössmann.

Oil of cassia was agitated with a concentrated solution of bisulphite of ammonia. The crystalline paste must be purified by washing with alcohol of spec. grav. 0·863 to 0·833. In other respects the author proceeded as in the preparation of amarine and lophine. He distilled with lime, and obtained an oily distillate, which consists of a new fluid base, hydrocarbons, amongst others benzole, and unaltered cinnamic aldehyde. The crude product is washed with a dilute solution of potash until all the ammonia is removed, and the fixed alkali is then got rid of by means of hot water. It is then rectified in a current of hydrogen. The base passes over between 284° and 302° F.

In the pure state the base is oleaginous, and at first colourless, but soon acquires a yellow and reddish colour by the action of air and moisture; it is readily soluble in alcohol and æther, but dissolves with more difficulty in water, has an alkaline reaction, and smells slightly like cinnamon-oil; with a moderately concentrated alcoholic solution of perchloride of platinum, it solidifies into a yellow crystalline paste, which dissolves with ease in ordinary alcohol. The salts partake of the property of the base, of altering readily under the influence of the air, especially when dissolved in water or alcohol; in this way a red colouring matter is principally formed, which adheres strongly to the salts, which are of themselves difficult to crystallize, and can be only got rid of by a great loss of material. The platinum compound, on the contrary, may be prepared with ease in any quantity.

Muriate of triphenylamine is obtained by the contact of the base with concentrated muriatic acid. An oil is obtained, which forms colourless crystals when poured over with alcohol of spec. grav.

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0·815; these must be washed with absolute alcohol. This salt forms shining laminæ with a slight reddish appearance; it is tolerably stable when kept from air and moisture, dissolves easily in water and ordinary alcohol, and with more difficulty in absolute alcohol and anhydrous æther; when aqueous æther is poured over it, it separates in a substratum as an oily liquid, and only dissolves again in it with the aid of alcohol. By the access of air it is rapidly altered in these solutions, and can only be prepared again in a crystalline form by being kept from the air over sulphuric acid, or under the air-pump. This muriate forms with perchloride of platinum a *double salt* of the formula $C^{36}H^{16}NCl+PtCl^2$, which is thrown down as a dark yellow flocculent precipitate, when a freshly-prepared solution of the muriate in strong alcohol is treated with a moderately-concentrated solution of perchloride of platinum. In alcohol of spec. grav. 0·876 to 0·863 the compound dissolves readily, and then forms a dark red solution, presenting a deceptive resemblance in colour to a solution of chloride of cobaltamine; when evaporated over sulphuric acid, it crystallizes in glassy forms, belonging to the regular system, of a chestnut-brown colour, and 0·3 to 0·5 millim. in size.

If the solution of the *pure* base be precipitated with a perfectly neutral alcoholic solution of perchloride of platinum, another platinum salt is obtained. This is pale, voluminous, granular-crystalline, and dissolves as readily as the first compound in water and alcohol; with this also it partakes of the property of easily attracting moisture when exposed to the air in a freshly-precipitated state, but when once dried it is unalterable. It has the formula $C^{36}H^{15}N+PtCl^2$.

The *oxalate* of this base crystallizes in needles, which attract moisture from the air.

By treating the pure base with iodide of æthyle in sealed tubes at 212° F. and subsequent treatment of the product, the author obtained a new base, the platinochloride of which has the formula $C^{40}H^{20}NCl+PtCl^2$. The base of this salt is therefore increased by C^4H^4, or æthyle has displaced 1 equiv. H.

From this the author concludes that the first base is a nitrile base, and has the formula—

$$\left.\begin{matrix}C^{12}H^5\\C^{12}H^5\\C^{12}H^5\end{matrix}\right\}N=\text{triphenylamine.}$$

The second base is an ammonium in which the fourth equivalent of hydrogen is replaced by the radical æthyle=C^4H^5. It is consequently triphenylæthylammonium—

$$\left.\begin{matrix}C^{12}H^5\\C^{12}H^5\\C^{12}H^5\\C^4\ H^5\end{matrix}\right\}N.$$

Liebig's *Annalen*, c. p. 57.

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On Gold in the Form of Malleable Sponge.
By D. Forbes, F.G.S.*

Of late years, gold in a peculiar state of aggregation has been imported from America for the use of the dentists, and sold at prices between from £7 to £8 per ounce. The gold is in the form of flat cakes, about two-tenths of an inch thick, and has a reddish-brown colour and peculiar spongy texture.

By the force of the fingers it can be welded or kneaded into a pellet without crumbling, and becomes by the pressure of a tool nearly as solid as ordinary gold. It is therefore well adapted for dental purposes.

The process by which it is said to be made is patented in America, and consists in repeatedly dissolving, precipitating, amalgamating, heating, &c., so extraordinary that it is probably only put forward to deter others making it. On trial, gold of a similar spongy character was obtained by the following method:—

Gold free from copper is dissolved in nitrohydrochloric acid, keeping an excess of gold in the solution towards the close of the operation, so as to get rid of all nitric acid and avoid subsequent evaporation; any chloride of silver present is filtered off. The solution of gold is now placed in a flat-bottomed vessel and heated, and a strong solution of oxalic acid added; in a few hours the whole gold is deposited, and the supernatant liquid may be decanted off, taking care all the time not to disturb the gold at the bottom, and the vessel is then several times filled up with boiling water and decanted until the last washings contain no more oxalic acid.

The gold is now carefully slipped on to a piece of filtering-paper, and by means of a spatula gently pressed into the form of the desired cake, but somewhat thicker; it is then removed to a porcelain crucible, and heated for a short time somewhat below a red heat, when it shrinks in dimensions, becomes coherent, and is similar to the American product in properties.

As the American gold is of a reddish hue, it is probably precipitated by protosulphate of iron, and not by oxalic acid.

On the Decomposition of Nitrate of Potash by Charcoal.
By A. Vogel, Jun.

The author has studied the behaviour of charcoal to nitrate of potash at various high temperatures. He obtained the following results:—

1. The oxidation of carbon mixed with nitrate of potash takes place completely and without incandescence at a temperature which scarcely exceeds that of fusing nitrate of potash.

2. The carbon is oxidized in this process to carbonic acid, and never to carbonic oxide gas.

* Communicated by the Author.

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3. The nitric acid is decomposed into nitrogen, nitric oxide, and nitrous acid, according to circumstances.

4. According to the conditions of temperature and the relative quantities of carbon and nitrate of potash, the potash occurs in the residue after the process of decomposition as nitrate and carbonate of potash, accompanied by undecomposed nitrate of potash.

5. These processes are effected according to the following equations:—

a. Residue, nitrite of potash.

1 equiv. $KO\,NO^5 + 1$ equiv. C.

$$\left.\begin{matrix} KO\,NO^5 \\ C \end{matrix}\right\} = KO\,NO^3 + CO^2.$$

b. *α.* Residue, carbonate of potash; gaseous mixtures, consisting of carbonic acid and nitrogen.

2 equivs. $KO\,NO^5 + 5$ equivs. C.

$$\left.\begin{matrix} 2(KO\,NO^5) \\ 5C \end{matrix}\right\} = 2(KO\,CO^2) + 3CO^2 + 2N.$$

β. Gaseous mixtures, consisting of carbonic acid and nitric oxide.

2 equivs. $KO\,NO^5 + 3$ equivs. C.

$$\left.\begin{matrix} 2(KO\,NO^5) \\ 3C \end{matrix}\right\} = 2(KO\,CO^2) + CO^2 + 2NO^2.$$

The latter process only occurs subordinately in company with the others.

6. Carbonic oxide gas does not exert a decomposing action upon fusing nitrate of potash; but in the nascent state, in a mixture of oxalate of potash and nitrate of potash, becomes oxidized to carbonic acid at a temperature at which oxalate of potash itself is quite stable.

7. For the preparation of chemically-pure nitrite of potash, the process of reducing nitrate of potash by charcoal is to be preferred to the method hitherto employed, of calcining nitrate of potash by itself.

8. In the detection of small quantities of carbon by the formation of carbonate of potash, by means of fusion with nitrate of potash, an excess of the latter is to be avoided, as with an excess of nitre no carbonate of potash is formed, but only nitrite of potash.—*Abhandl. der Königl. bayer. Akad. der Wiss.; Journ. für Prakt. Chem.*, lxviii. p. 65.

On the Compounds of Tantalum with Fluorine. *By* H. Rose.

Hydrated tantalic acid dissolves even at ordinary temperatures in aqueous hydrofluoric acid, forming a clear fluid. The solution does not become turbid by heat, or by the addition of sulphuric acid. The solution, mixed with sulphuric acid, may be concentrated by evaporation, without separation of tantalic acid. It is only when it has been reduced to a small volume that it becomes somewhat tur-

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bid; but by further evaporation, when the sulphuric acid has become concentrated, the separated tantalic acid is again dissolved by the aid of heat.

If the solution of tantalic acid in hydrofluoric acid be heated and evaporated, perfluoride of tantalum is volatilized; from the residue a white vapour of perfluoride of tantalum is evolved by calcination, and tantalic acid remains. Even when sulphuric acid is added to the solution of tantalic acid in hydrofluoric acid, the entire quantity of tantalic acid cannot be reproduced by evaporation and driving off the sulphuric acid; the loss, however, is but small.

Calcined tantalic acid does not dissolve in hydrofluoric acid. When it is evaporated therewith and mixed with sulphuric acid, and the dry residue calcined in an atmosphere of carbonic acid, the entire quantity of tantalic acid employed is reproduced. When mixed with fluoride of ammonium and calcined, however, calcined tantalic acid is completely volatilized.

Perfluoride of tantalum, as already pointed out by Berzelius, has a remarkable tendency to combine with metallic fluorides to form double compounds. With fluoride of potassium it combines in several proportions; Berzelius also obtained no simple compound, but mixtures or mixed crystallizations of $KF + TaF^3$ and $KF + 2TaF^3$. But with fluoride of sodium the compound $NaF + TaF^3$ is obtained, which certainly does not correspond to the neutral tantalate of soda. —*Bericht der Akad. der Wiss. zu Berlin*, 1856, p. 436.

ANALYTICAL CHEMISTRY.

Quantitative Determination of Boracic Acid. By A. Stromeyer.

For the quantitative determination of boracic acid, Berzelius has recommended the borofluoride of calcium. Rose and Weber tested this process, and obtained unfavourable results. The author has found that correct results may be obtained in this way, by taking care that the boracic acid is combined with alkali, especially potash, at least 1 atom of which must be present to 1 atom of boracic acid.

The author's process is as follows. In the first place, the boracic acid is combined with a sufficient quantity of potash; pure hydrofluoric acid is then added in excess, and the whole is evaporated to dryness, during which vapours of the excess of hydrofluoric acid reddening litmus-paper, must be evolved. At first, gelatinous borofluoride of potassium is produced, which subsequently forms small, hard, transparent crystals. The dry saline mass is then stirred up at the ordinary temperature with a solution of acetate of potash of 20 per cent., and left to stand for some hours, when the fluid is passed through a weighed filter, and this is repeated several times, after which the salt is also put upon the filter, and washed with the solution as long as the filtrate gives a precipitate with chloride of calcium. The acetate of potash is then washed away with alcohol of spec. grav. 0·851, and the salt is dried at 212° F. A solution of acetate of potash of the above strength dissolves chloride of potassium and nitrate

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and phosphate of potash, and, although with some difficulty, even sulphate of potash. The presence of the ordinary acids therefore is not injurious in this method. Soda-salts also dissolve in it, and the experiments made by the author with borax show that their presence does not affect the exactitude of the results. Nevertheless they are to be avoided if possible, as fluoride of sodium is difficult of solution. Other bases, however, must be previously separated, which will be easily done in all cases by boiling or fusing the borates with carbonate of potash. Magnesia is not quite insoluble in water, and some of it is therefore obtained in the alkaline liquid. In the neutralization with hydrofluoric acid, it separates as insoluble fluoride of magnesium, which may either be separated by filtration before any more acid is added, or its quantity may be determined afterwards by washing the filter with boiling water, by which the borofluoride of potassium may be extracted without difficulty. It is as well always to do this in order to be certain of its purity. The solution should give no precipitate of silica with ammonia. As observed by Berzelius, this salt undergoes no alteration by being heated with solutions of the alkalies, whilst by this means silicofluoride of potassium is decomposed with separation of silica. If therefore the salt is contaminated therewith, it may be dissolved in boiling water, precipitated with ammonia, filtered, and again evaporated and lixiviated with acetate of potash and alcohol.

The borofluoride of potassium obtained takes up very little room. The author filters through funnels made of gutta-percha or india-rubber, because the fluoride of calcium running away attacks glass. The evaporation of the borate of potash with hydrofluoric acid is effected in vessels of silver or platinum.

The author makes his own apparatus for the preparation of hydrofluoric acid. A piece of lead-pipe of 2 inches in diameter and a foot long is buried vertically in a pail full of sand, and filled with sand to within half an inch of the margin, and the empty part is scraped bright with a knife. It is then filled with molten lead, which is poured on in considerable quantity, the excess of lead being conducted off by a furrow in the sand. In this way the pipe is closed with lead at one end. This pipe serves as a retort, and easily holds 6 oz. of fluor spar with 12 oz. of sulphuric acid. After the acid has been sufficiently mixed with the powder by means of an iron rod, it is allowed to stand for several days, in order that the intermixed silica may be evolved as fluoride of silicon. The leaden vessel is then closed with a cork, through which passes a leaden tube of half an inch in diameter. The cork is coated with a lute of cheese and lime, and after this is hardened, a roll of paper is pasted round, which is then filled with plaster of Paris, until a thick head is obtained, and in this way a complete closure. During the application of heat the vessel is placed in an oblique position upon a couple of bricks, and heated with charcoal. An india-rubber tube is attached to the half-inch lead-pipe, and this is brought close over the surface of the water. The acid is received in vessels of india-rubber.—Liebig's *Annalen*, c. p. 80.

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On the Determination of Phosphoric Acid in the Presence of Iron. *By* R. Arendt *and* W. Knop.

When phosphoric acid is to be removed by means of acetate of uranium from a solution which contains iron, the precipitate of phosphate of uranium and ammonia has a different nature according to the quantity of iron present. If the amount of iron be very small, not greater for example than occurs in the ashes of plants, it does not alter the nature of the precipitate. If its amount be more considerable, the precipitate, which in itself is slimy, becomes dense and heavy. We have investigated the causes which produce this modification, and found that under the circumstances described the precipitate takes up several parts per cent. of phosphate of iron.

The properties possessed by the precipitate containing iron present advantages in qualitative investigations. Thus the precipitate settles very well, and under all circumstances, be the amount of iron ever so large, it passes into solution up to a minimum, so that after treatment with acetate of uranium we have a solution free from phosphoric acid, which contains all the bases, and from which, on the addition of ammonia, oxide of uranium, iron, and alumina are precipitated. The hindrance which is offered by phosphoric acid to the testing of the alkaline earths is thus got rid of.

In quantitative determinations, on the contrary, the advantage of being able to weigh the precipitate directly would be lost; in this case we must determine its amount of iron separately.

Experiments which we have made with protoxide of uranium, however, appear to get over all the difficulties which are produced by the presence of much iron. If we add to a solution of calcined phosphate of uranium in muriatic acid a quantity of iron about equal to that of uranium, then add acetic acid and acetate of uranium to it, heat it to boiling, and put zinc foil into it, and then leave it standing for some time over the lamp, and afterwards for some hours in the cold, the muriatic acid is saturated by the zinc, whilst the acetic acid remains free. The fluid becomes filled with a jelly of protophosphate of uranium, which may be very easily washed. The iron passes over into the washing water, which contains no phosphoric acid, whilst the washed precipitate contains no iron.

The same object is attained by the employment of protochloride of uranium from the first*.—*Chemisches Centralblatt*, Nov. 5, 1856, p. 803.

On the Determination of the Value of Madder and Garancine. *By* H. Hannes.

For the determination of the colouring power of madder and garancine, which he manufactures, the author adopts the following process:—

* The yellow precipitate of phosphate of uranium, as repeatedly stated in former papers (see Chem. Gaz., vol. xiv. p. 467), is difficult to wash. By the addition of a drop or two of chloroform and short boiling, this disadvantage entirely disappears immediately. We do not yet know, however, whether the composition is not altered thereby.

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The samples of garancine or madder to be tested are first finely powdered, and their amount of water determined; 0·1 grm. of each powdered sample is then left standing for twelve hours, with frequent shaking at about 50° to 56° F., with

2·3 grms. of solution of caustic potash (spec. grav. 1·335) and 10 cub. centims. of distilled water;

2·3 grms. of solution of carbonate of potash (Liq. kali carb. puri of spec. grav. 1·332) and 10 cub. centims. of distilled water; and

2·3 grms. of liquid ammonia (spec. grav. 0·960) and 10 cub. centims. of distilled water,

in well-stoppered vessels; each fluid is then brought up to 300 cub. centims. with distilled water, and the filtrates of the fluids are compared according to the solvent, by means of two burettes.

2·42 grms. of A-garancine lost by drying 0·31 grm.; 3·10 grms. of B-garancine, on the contrary, 0·85 grm.

0·1 grm. of A-garancine was treated with carbonate of potash as above, and 15 cub. centims. of the filtrate were compared with the same quantity of the filtrate from B-garancine treated in the same way; it appeared that the 15 cub. centims. of the A-garancine still required 10 cub. centims. of distilled water to furnish the same tint as the 15 cub. centims. from the B-garancine.

In the treatment with caustic potash, the 15 cub. centims. of A-garancine required to be diluted with 9·8 cub. centims. of water; in the treatment with ammonia it took 9·6. As at least 280 cub. centims. of each fluid are retained, the results are easily checked; the volatility of the ammonia then causes a somewhat different result if the operation be not carried on with sufficient care, but the error is not of such importance as it would appear.

The average of the three experiments gave $\frac{45+29\cdot4}{3}=24\cdot8$. The value of the A-garancine is therefore 24·8, and that of the B-garancine 15, for equal weights, without reference to the amount of water contained in them; if this be taken into consideration according to the values found, we get—

$$\frac{2\cdot11\,.\,100}{2\cdot42}=87\cdot23\ldots\ldots;\quad \frac{2\cdot25\,.\,100}{3\cdot10}=72\cdot58;$$

$$\frac{87\cdot23\,.\,24\cdot8}{100}=21\cdot63304\ldots;\quad \frac{72\cdot58\,.\,15}{100}=10\cdot8870.$$

According to this, the effective value of the A-garancine would be 21·633, and that of the B-garancine 10·887, with the employment of equal weights, and the price of the two may therefore readily be ascertained in accordance with their value.—Dingler's *Polytechn. Journal*, cxlii. p. 215.

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CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Production of Nickel at the Aurora Works near Gladenbach. By Dr. E. Ebermaier.

The Aurora Works are situated near Gladenbach in Hesse, three miles from Marburg; the ores occur quite in the vicinity of the works. The author studied the process on the spot, and performed the investigation in Wöhler's laboratory.

The ores which are worked at the Aurora Works are an amygdaloidal trap, in which copper containing nickel and iron pyrites is disseminated. The author submitted a large portion of these disseminated ores to chemical examination, and obtained the following results:—

Iron.....	40·727 per cent.	Cobalt.....	traces
Copper ..	3·412 ...	Sulphur	48·819 per cent.
Nickel....	1·733 ...	Rock and loss	5·309 ...

From these results it appears that the ore is a mixture of iron and nickel pyrites: 3·412 per cent. of copper require for the formation of copper pyrites, in accordance with the formula $Cu^2S + Fe^2S^3$, 3·014 per cent. of iron and 3·444 per cent. of sulphur.

There consequently remains 37·613 per cent. of iron for the formation of iron pyrites, which require 43·086 per cent. of sulphur.

For the formation of nickel pyrites, NiS, the 1·733 per cent. of nickel found require 0·936 of sulphur.

According to these calculations, we obtain for sulphur—

In the copper pyrites	3·444 per cent.
In the iron pyrites.....	43·086 ...
In the nickel pyrites.....	0·936 ...
	47·466 ...
Found....	48·819 ...

But if we were to suppose that there is a nickel pyrites analogous to the iron pyrites, and therefore constituted according to the formula NiS^2, or that iron is displaced by nickel in the iron pyrites, another 0·936 per cent. of sulphur would be required, and the calculated quantities would agree better with the found numbers.

The above-mentioned amygdaloidal trap, in which the ores are disseminated, is broken up into small fragments, and smelted in a furnace with coke and slag still containing nickel. By this means a crude regulus is obtained, which still contains much sulphur, but does not exhibit a definite composition.

The slag, on the contrary, is so definitely characterized, that an investigation of it appeared desirable. It has a perfectly glassy fracture, and may be drawn out into threads, which when kept warm do not break, and are coloured green by protoxide of iron. It only

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dissolves with difficulty in nitromuriatic acid, leaving a residue of silica, and has the following composition:—

Silica	47·207	24·511	=29·951 oxygen.
Alumina	11·64	5·44	
Protoxide of iron	26·509	5·884	
Peroxide of copper	0·147	0·029	
Protoxide of cobalt	trace	..	
Protoxide of nickel	trace	..	
Lime	9·117	2·592	=11·031 oxygen.
Magnesia	4·839	1·901	
Potash	0·896	0·152	
Soda	1·843	0·473	
	102·198		

From this composition it appears that the quantity of oxygen in the silica and alumina is three times that in the other bases, from which the formula

$$RO \begin{cases} SiO^3 \\ Al^2 O^3 \end{cases}$$

is derived, in which RO represents the mutually-replacing bases FeO, CuO, NiO, CoO, CaO, MgO, NaO, KO.

In this first fusion, a product containing a very large quantity of iron, and which very rapidly solidifies, sometimes collects in the hearth. When freshly fractured, the product has exactly the appearance of finely granular pig-iron; it consists of—

Iron	88·167	Copper	1·396
Nickel	4·854	Sulphur	4·045
Cobalt	0·051	Silicium	2·106

It also contained a small quantity of carbon, which is given off as carburetted hydrogen on treatment with muriatic acid.

The crude regulus obtained is broken up small, and roasted four or five times in parcels; it is then smelted in the same furnace with coke and the slags resulting from the first smelting which still contain some regulus.

The mass thus obtained has a gray colour with a reddish tinge, and a jagged fracture; it is very tough. It sometimes occurs distinctly crystallized; the piece at the author's command was beset on the surface with octahedra of 2 lines in length, which were furrowed on the surface, and covered with a coat of a dull gray colour.

This is due to oxidation, as was distinctly shown by analysis. Thus in the examination of the crystals covered with this coat, a loss was always experienced. When this loss was calculated as oxygen, and the composition of the crystals compared with that of fragments from a fresh fracture, and calculated for 100 parts, a similar result was found. This is as follows:—

Sulphur	11·080	Nickel	35·513
Copper	26·579	Cobalt	0·621
Iron	26·072		

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It is remarkable in this case, that with such a beautiful crystallization no formula can be calculated, from the small amount of sulphur.

This regulus also does not appear to be always of the same composition, as was shown by an analysis made some years ago, which gave—

Sulphur	24	Iron.....	34
Copper	18	Nickel.....	24

The slag of the second smelting is as definitely characterized as the former; it possesses almost a fine conchoidal fracture and a greenish-black colour, and is very hard and brittle. In the fused state it is much more fluid than the first, may be drawn out into threads, which however break when kept warm, and solidifies rapidly. It is also difficult of solution in nitromuriatic acid, leaving a residue of somewhat coloured silica. The quantitative proportion of the constituents is as follows:—

Silica.....	39·368	20·541	=24·973 oxygen.
Alumina	9·696	4·432	
Protoxide of iron..	36·859	8·881	
Protoxide of copper	0·521	0·105	
Protoxide of nickel	1·137	0·242	
Protoxide of cobalt	trace	..	
Magnesia	6·871	2·699	=13·184 oxygen.
Lime.....	5·865	1·667	
Soda.....	0·994	0·255	
Potash	0·207	0·035	
	101·518		

From the proportion of the oxygen in the bases to that of the silica and alumina, is derived the formula $3RO+2\left\{\begin{matrix}SiO^3\\Al^2O^3\end{matrix}\right.$.

The regulus resulting from the second fusion is heated in a suitable copper furnace, the fuel employed being coke. The iron contained in it passes into the slag as protoxide, and a regulus is obtained which is free from iron, and contains 60 per cent. of nickel, copper, and a little sulphur. This regulus is the last product which is prepared at the smelting works; this is supplied to the nickel manufactory in Cassel, where it is freed from sulphur by a process which is a secret of the factory, and then comes into commerce as cupreous nickel, for use in the manufacture of German silver.

The slag has nearly the same properties as the preceding ones. It is however much more fluid, and solidifies far more rapidly. Of all the slags it dissolves with the greatest difficulty in acids, and leaves a residue of very loose granular silica still containing oxide of iron and alumina, which, like the preceding ones, must consequently be decomposed by fusion with carbonate of soda. Its composition is as follows:—

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Silica	36·291	18·843	=23·849 p. c. oxygen.
Alumina	10·71	5·006	
Protoxide of iron	48·691	10·807	
Peroxide of copper	1·074	0·216	
Protoxide of nickel	2·142	0·456	
Protoxide of cobalt	0·262	0·056	=11·849 p. c. oxygen.
Magnesia	0·309	0·121	
Lime	0·68	0·193	
Alkalies	traces		

Like the preceding, this slag therefore also corresponds with the formula $3RO+2\left\{\begin{matrix}SiO^3\\Al^2O^3\end{matrix}\right.$

Berg- und Hüttenmann. Zeitung, 1856, No. 36.

Preparation of the Red Colouring Matter from Madder.
By E. Schwarz.

For the separation of the pure red colouring matter of madder (alizarine) from resin, the author spreads the triturated extract of the madder-root in thin layers upon filtering-paper, and lays the whole upon a thin iron plate furnished with a handle, so that it may be at pleasure brought near to or removed from a pan of red-hot charcoal. The paper serves to regulate the heat, as it must remain uninjured during the operation.

The mass soon becomes fluid, and then separates into two very different parts: one of these penetrates the paper in the form of a dark brown substance, and at the same time the other covers the paper as a down of reddish-yellow needles, which may be easily removed when cold.

The heat must be regulated so that only a slight white vapour is evolved from the fusing extract, and not a reddish one, for in the latter case the sublimed product will gradually disappear.

The crystals obtained by this process are completely purified from the brown resin, for if they be triturated and again sublimed in the same way, they leave no coloured trace upon the paper. These crystals are slightly soluble in hot water, but readily in alcohol, æther, caustic alkalies, the oils, and concentrated sulphuric acid; they therefore behave exactly like the resins with these agents.

From the results given by this sublimed product in dyeing, it may be regarded as the red colouring matter of madder in a state of the greatest purity. This is also proved by its constant colouring power.

As, however, this substance is only diffused in water with great difficulty, it must be first of all dissolved in a very little boiling alcohol, and this solution diluted with a sufficient quantity of water. In this way a milky bath is obtained, which readily parts with all its colouring matter to mordants.

The brown resin remaining in the paper retains a considerable quantity of the red colouring matter, but the colours which it produces in dyeing are duller and more yellowish than those furnished by the extract of madder from which it is derived.

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The brown extract which accompanies the red colouring matter may also be got rid of from the alcoholic extract of madder. The colouring matter dissolves more readily than the resin in boiling water containing alum. 10 grms. of alcoholic extract of madder were boiled for half an hour in 1 hectolitre of water free from lime; the next day the coloured water, at the bottom of which light rose-coloured flakes were swimming, was decanted. This operation was repeated fifteen times. The brown residue of this treatment only contains very little of the red colouring matter. From this it follows, therefore,—

1. That the red colouring matter of madder is obtained in the purest state when an alcoholic extract of madder, possessing thirty-five times the colouring power of the root, is sublimed upon paper.

2. That the brown resin may be separated from an alcoholic extract of madder by frequent treatment with boiling water in which a little alum is dissolved.

3. That the brown resin with which the colouring matter is combined in the madder retains a portion of the colouring matter after dyeing with madder, and thus contributes to loss.—Dingler's *Polytechn. Journal*, cxlii. p. 135.

On the so-called Permanent White, or Blanc-fix (*Sulphate of Baryta*). *By* S. Gompertz.

Sulphate of baryta is manufactured under the name of permanent white or *blanc-fix*, in Berlin, Schweinfurt, Mannheim, Mayence, Cologne, and other places in North Germany, and is meeting with a daily increasing adoption as a water-colour in various arts. The dazzling snow-white of this colour can be produced by no other substance; it is indifferent to the action of air, light and heat; is not darkened by the influence of sulphuretted hydrogen or other gases; and when laid on thin in several coats with clear size colour, it has a body which approaches most closely to that of the purest white lead of Krems. Its cost of production being more than 50 per cent. less, and its specific gravity lower, its cost when employed is hardly a third of that of white lead.

To the manufacturers of paper-hangings this white offers the essential advantage that it acquires a satiny lustre with the brush, both with and without talc, which is otherwise unattainable, and resists damp. Dazzling-white satin-papers, which now occur in the shops at astonishingly low prices, are made with this colour. Lastly, it is adapted for mixed colours, equally from its neutrality and inalterability, and from its peculiar property of leaving the primitive tone of colour unaltered. Mixed with a bright red-lake, it gives the most beautiful rose colour, and with prussian blue the most lively pale blue. Every one who has to do with mixed colours knows the difficulty of obtaining vivid pale rose and blue tints.

Baryta-white is obtained partly from heavy spar itself, by reducing this when finely powdered to sulphuret of barium by means of charcoal, decomposing the sulphuret into chloride of barium and sulphuretted hydrogen by muriatic acid, and precipitating the baryta-white from the solution of chloride of barium by diluted sulphuric

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acid, or a sulphate, such as sulphate of soda; and partly from Witherite (carbonate of baryta), which has hitherto only been procured from England, in which case the mineral is converted directly into chloride of barium by dilute muriatic acid, and then treated as above. The manufacture of the baryta-white from the latter mineral is more costly than from the former, although it is simpler on the whole, and the colour obtained from Witherite fetches a higher price. According to the author, however, it possesses essential advantages over that obtained from heavy spar. It is of a more beautifully lustrous white, requires less sizing, and is completely free from acid; whilst the white prepared from heavy spar always contains acid, and evolves acid by standing, so that it destroys the adhesive medium. The cause of this behaviour in the colour prepared from heavy spar is probably, according to the author, its always containing a little (0·25 to 1 per cent.) finely-divided sulphur, which gradually becomes oxidized when exposed to the air.

Baryta-white is prepared from Witherite in England, France and America, but in Germany, as far as the author is aware, only in Cologne. The product prepared at the latter place is the best; it is of a dazzling white, free from acid, and only contains as much water as is necessary to enable it to be readily diluted afterwards by an addition of water. The higher price of the Cologne product is thus to a certain extent reduced in comparison with that of other manufactories, which usually contains more water. A certain degree of dehydratation must not be exceeded in the preparation of the white, as it then mixes with water with difficulty, and loses both in body and fineness. As soon as cracks appear in the doughy mass, which has been left to stand quietly, the extreme degree of dehydratation is exceeded, and the mass must be again kneaded with water.—*Monatsschrift des Gewerbevereins zu Köln*, 1856, p. 34.

Theoretical and Practical Researches upon the Fixation of Colours in Dyeing. *By* F. Kuhlmann. (Third Part.)

The facts detailed in the former parts of this memoir* show that the fixation of colours in dyeing depends, if not exclusively, at least to a very great extent, upon a chemical action between the colouring matters and the stuffs, either in their natural state, or modified by their combination with other bodies, or by a peculiar molecular arrangement of their constituent principles. To establish this proposition as regards the combination of cellulose with nitric acid, it must be clearly shown that this acid does not act in dyeing by becoming free, and acting in this state upon the colouring matters. To remove all objections in this respect, it would be sufficient to argue that tissues, nitrated to different degrees, do not lose their property of being more combustible than ordinary tissues by dyeing. The author has also proved that pyroxylized stuffs do not take up more colour in acid than in alkaline baths, and that pyroxyline spontaneously decomposed attracts colours in both cases more energetically than ordinary cotton. He has proved these facts by dyeing

* Chem. Gaz., vol. xiv. pp. 192, 217.

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ordinary cotton, pyroxylized cotton, nitrated cotton, and spontaneously decomposed pyroxyline, without any mordant, in an acid solution of indigo and in an alkaline one of orchil; the characteristic properties of the vegetable fibre in its different states of combination were always manifested. Pyroxyline deprived of a part of its nitrous principles by spontaneous decomposition, and nitrated cotton, behave in tincture of safflower exactly as in that of Brazil-wood, madder, &c., whilst gun-cotton does not acquire colour in any case. It is therefore evident, that, by its combination with a definite proportion of nitrous principles, cellulose approaches the natural azotized substances in its properties of absorbing colours.

It cannot be absolutely established as a principle in dyeing, that the natural azotized tissues of animal origin have always a greater affinity for colours than non-azotized tissues. Wool does not take the colour of safflower with the same facility as cotton. This is also the case with nitrated wool; but the author has ascertained that silk, treated with nitric acid, although quite deprived of free acid, attracts the colour of safflower with more energy than in its natural state, giving a scarlet colour like nitrated cotton; this property is not exhibited in the same degree by wool. In all his experiments he has found that wool is of all substances the least apt to acquire a greater disposition to absorb colouring matters by its immersion in nitric acid.

It must not be supposed that all artificial azotized bodies possess the property of attracting colours and assisting in fixing them upon tissues. Experiments with uric acid, nitrate of urea, and urate of potash gave no result. If, as regards safflower, the resistance of wool to the reception of this colour results from peculiar properties foreign to the composition, we must also attribute to the peculiar properties of uric acid, its incapability of serving to fix colours like the nitrous compounds.

Modifications in Molecular Arrangement.—Some years ago, an English manufacturer, Mr. Mercer, stated that cotton-stuffs gave richer colours by immersion, before the application of the mordant, in a concentrated solution of caustic soda. The author has proved the truth of this assertion; but the results obtained are far from being comparable with those produced by the combined action of nitric and sulphuric acids. The phænomenon has been attributed to a simple approximation of the fibres of which the tissue was composed. Tissues treated with a caustic alkali contract in every direction, but the author considers this explanation as quite inadmissible in cases where the intensity of the colours is enhanced by other reactions, especially that of the spontaneous decomposition of pyroxyline. Without absolutely attributing to this cause the intensity of the colours acquired by cotton prepared with potash or soda, it may easily be admitted that many modifications of the nature of tissues by energetical chemical agents, may give them a greater aptitude for the absorption of colours.

The author has made numerous experiments in dyeing with cotton-stuffs altered by the action of various chemical agents, with or

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without the assistance of heat. The tissues were altered by means of chlorine, muriatic acid, and hydrofluoric acid; no result was obtained; which leads to the conclusion that all alterations are not adapted to increase the absorptive properties of cotton. The action of concentrated sulphuric and phosphoric acids gave more favourable results. The tissues contract, as by the action of alkalies, and acquire a certain translucency, a circumstance which may to a certain extent explain their ready permeability by coloured solutions; but in presence of the numerous facts indicated in this memoir, in which these effects are not produced, it appears to the author to be more logical to suppose, in general, that a different molecular arrangement in the material to be dyed is the essential cause of the results observed, even when there is no change in the chemical composition. Here the tissues contract and acquire a slight translucency; it is evident that in these various circumstances the cellulose is modified in its chemical nature, and has a tendency to become converted into dextrine and glucose; and even if we suppose that the composition of the cellulose is unchanged, we may suppose very different properties in isomeric bodies. In these cases a different molecular arrangement may give rise to a new chemical combination; and the greater intensity of colour in dyeing should rather be attributed to a different chemical combination than to the purely physical state of the material. How many isomeric bodies there are amongst organic compounds, which nevertheless exhibit different properties as regards their combination with other bodies.—*Comptes Rendus*, Nov. 10, 1856, p. 900.

On an Ammoniacal Extract of Madder for Dyeing Purposes.
By J. H. Woolbert.

The extract of madder, prepared according to the following prescription, is applied to the stuff thickened with dextrine, or some other substance. For red or rose colour, acetate of alumina is employed as a mordant; for violet or black, acetate of iron.

1 kilogrm. of madder, reduced to the finest powder, is macerated for twenty-four hours with a mixture of 1 kilogrm. of liquid ammonia of 22° B. and 100 grms. of alcohol. The mixture is then diluted with 1 kilogrm. of water, and heated for thirty to forty minutes over a weak fire, and stirred at the same time. After its removal from the fire, 100 grms. of alcohol are added; the mixture, when it has become uniform, is put into a linen bag, and the fluid, which forms the desired extract, is pressed out. The madder remaining in the bag may be treated again in the same way, after which it is macerated with 1 kilogrm. of ammoniacal water and again pressed. The fluid thus obtained is used instead of water in the treatment of subsequent portions. The extracted madder may still be employed in the ordinary madder-dyeing, by boiling it previously with an equal weight of sulphuric acid of 8°, and then freeing it from the acid by washing with water, to which towards the end of the operation some carbonate of soda is added.—*Polytechn. Centralblatt*, 1856, p. 1471.

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THE CHEMICAL GAZETTE.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

Researches on the Silicates. *By* E. FREMY.

THE author's previous researches on the metallic acids led him to think that the two isomeric states of silica, which establish such great differences between quartz and silica chemically prepared, would also exercise some influences upon the capacity of saturation of this acid, that is to say, upon its tendency to retain more or less of base; the following facts confirm this supposition.

When hydrated silica is brought into contact with alkaline bases, and the combination takes place at a low temperature with an excess of acid, a first series of silicates is obtained, presenting the following characters:—The salts are soluble in water and crystallizable, but they may be obtained isolated by precipitating them with alcohol, or by evaporating their solution, which furnishes on cooling a gelatinous mass, which may be easily pressed out. These silicates are represented by the formulæ—

$$(SiO^3)^3, KO + Aq, \qquad (SiO^3)^3, NaO, 20HO.$$

By the action of heat they undergo a remarkable modification. If they be treated with water after a slight calcination, it is found that the saline group forming them is destroyed; they are not dissolved, but leave an insoluble siliceous deposit, and yield nearly pure alkali to the water.

The state of the silica thus produced appears to depend on the temperature at which the modification of the salt is produced; when the calcination has been carried to a bright red heat, the silica obtained scratches glass, withstands the action of acids, and only dissolves in fused alkalies, thus presenting some of the characters of quartz. If the salt has been exposed to a lower temperature, the silica retains its solubility in dilute alkaline solutions; it retains no traces of alkali and is chemically pure. This decomposition of the silicates may be attributed to a phænomenon of dehydratation, or to an isomeric modification of the silica, which, approaching the state of quartz, would gradually lose its affinity for bases.

We only possess very vague notions upon the conditions which have allowed potash to escape from the felspathic rocks and penetrate into plants. The preceding observations appear to throw some light on this important natural phænomenon; they show that there

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exists a class of alkaline silicates comparable with those which may be furnished by the felspars, presenting so little stability as to allow the deposition of silica under the least energetic influences, and thus set free the alkali. This is also the cause of the influence exerted in agriculture by burnt clays.

The above-mentioned silicates may become modified, even at ordinary temperatures, by the influence of an excess of base, and converted into a new series represented by the following formulæ:—

$$(SiO^3)^3, 2KO + Aq, \qquad (SiO^3)^3, 2NaO + Aq.$$

These salts are more stable than the preceding ones, but yet they abandon a portion of their base under the influence of heat. When the preceding salts are boiled with an excess of alkali, they give origin to a new series represented by the formulæ—

$$(SiO^3)^3, 3KO + Aq, \qquad (SiO^3)^3, 3NaO + Aq.$$

These silicates, like the preceding, are uncrystallizable, but they are much more stable; they are not decomposed by calcination, and retain their solubility in water, even when they have been heated to redness.

By calcining the preceding salts with an excess of alkali in a silver crucible, or by acting upon quartz with potash or soda in fusion, another series of silicates is formed; these are very stable, and crystallize readily. The silicate of soda belonging to this series, which may be obtained in large crystals, is represented by the formula—

$$(SiO^3)^3, 4NaO, 26HO.$$

Silica therefore belongs to that class of acids of which the capacity for saturation is variable, and dependent in some degree upon the quantity of base presented to them. These acids are really *polybasic*; and to get an exact idea of their capacity for saturation, they must be followed in the saline development which they may be made to undergo by an energetic base.—*Comptes Rendus*, Dec. 22, 1856, p. 1146.

Note on the Oxalate of Manganese. *By* Henry Croft, D.C.L., F.C.S., Professor of Chemistry, University College, Toronto*.

In Gmelin's 'Handbuch,' vol. iv., the oxalate of the protoxide of manganese is described as having been obtained by Graham, combined with 5 equivs. (24·16 per cent.) of water, by precipitation of a solution of 1 part of manganese-salt in 100 of water, by means of oxalate of potash; and this compound is stated to lose no water at 212° F. Nothing is said with regard to the amount of water in the precipitate obtained from concentrated manganese solutions by oxalic acid.

There is evidently some error in the above statement, for the formula $MnO, C^2O^3 + 5HO$ requires 38·60 per cent. of water, and $MnO, C^2O^3 + 3HO$ requires 27·39.

In the 89th volume of the 'Annalen der Chemie und Pharmacie,'

* Communicated by the Author; having been read before the Canadian Institute, Dec. 20, 1856.

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Hausmann and Löwenthal give an analysis of the oxalate obtained by acting on freshly-precipitated carbonate of manganese with oxalic acid, from which they deduce the formula $MnO, C^3 O^3 + 2HO$ for the salt dried at 212° F.

The following experiments were made for the purpose of explaining the discrepancy.

Strong solutions of sulphate of manganese were precipitated by saturated solutions of oxalic acid; a granular white precipitate was obtained in both cases, which did not lose water at 212° F. I. and II.

Similar solutions were mixed when boiling. III.

Sulphate of manganese was dissolved in 30 parts of water, and oxalic acid added, a light pinkish crystalline precipitate was formed after a time, which in the course of a few days changed into a perfectly white granular powder. IV.

Sulphate of manganese was dissolved in 30 parts of water, and a solution of oxalate of potash added; a light pinkish crystalline precipitate gradually formed, having the appearance and lightness of benzoic acid; it absorbed and retained water like a sponge, and remained unchanged in the air at ordinary temperatures, but became perfectly white at 212° F. V.

Sulphate of manganese was dissolved in 100 parts of water, and oxalate of potash added; the same pink salt was obtained. VI. This should be the compound described by Graham, with 5HO.

White Salt.

I.	1·391 grm.	gave	0·5890	$Mn^3 O^4$ =	39·38	per cent. MnO
II.	1·292	...	0·5566	...	40·07	...
III.	1·717	...	0·7510	...	40·68	...
IV.	1·295	...	0·5545	...	39·83	...
				Mean.....	39·99	

The formula $MnO, C^3 O^3 + 2HO$ requires 39·72.

Pink Salt.

V.	1·0575 grm.	gave	0·418	$Mn^3 O^4$ =	36·77	per cent. MnO
	1·3700	...	0·536	...	36·79	...
VI.	1·4395	...	0·567	...	36·64	...
	1·5300	...	0·597	...	36·39	...
				Mean.....	36·62	

1·5300 heated to 212° F. lost 0·134 HO = 8·75 per cent. HO, and became perfectly white.

The formula $MnO, C^3 O^3 + 3HO$ requires 36·09 per cent. MnO, and 1. equiv. of water would..... = 9·09 per cent.

The red oxide of manganese is obtained by heating this salt, in a crystalline form; the complete conversion of the protoxide into the red oxide is only effected after a rather long roasting.

Burin du Buisson is of opinion that pure salts of the protoxide of manganese are colourless when in an anhydrous state, but reddish when hydrated, while Reithner and others ascribe the red colour to

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the presence of a salt of the sesquioxide. The pink colour of the above hydrate can scarcely be owing to the latter cause, inasmuch as the salt is produced both by oxalic acid and by oxalate of potash; and the salt with 2HO is generally obtained perfectly white. (This salt is described by Liebig as having a tinge of pink, but in my experiments it was always white.) The pink crystallized salt changes in a warm atmosphere, even when kept in a close vessel, into the white compound, evolving water.

The oxalate dissolves readily in a hot solution of oxalate of ammonia, and crystalline compounds can be obtained, as already described by Winkelblech: these crystalline crusts, however, seem to vary much in their composition, and are probably combinations of the true double salt with variable proportions of oxalate of ammonia, similar to the magnesia compounds lately described by Souchay and Leussen.

On Sulphobenzide. *By* Dr. H. Gericke.

The sulphobenzide which was employed in the following experiments was obtained by the treatment of benzine with anhydrous sulphuric acid. It crystallizes in beautiful, white, silky, strongly refractive, small, rhombic prisms, which fuse at 239° F. (usually at 150° F., as Cahours states), and solidifies again in a crystalline form at the same temperature, when small prisms are frequently formed. It is inodorous, tasteless, but little soluble in cold, and more readily in hot water. It is dissolved unchanged by dilute nitric acid with the assistance of heat, but decomposed by concentrated acid. By concentrated sulphuric acid it is blackened and dissolved; if this solution be diluted with water until the latter no longer produces a precipitate, and then saturated with carbonate of baryta, rhombic prisms of sulphophenylate of baryta, $C^{12} H^5 BaS^2 O^6$, are produced.

Sulphobenzide is not decomposed into sulphophenylate of potash and benzine by an alcoholic solution of potash even at 356° F. When heated with concentrated fuming nitric acid until its complete decomposition, sulphobenzide furnishes two bodies, namely binitrosulphobenzide and nitrosulphobenzide.

Nitrosulphobenzide, $C^{24} H^9 (NO^4) S^2 O^4$, is thrown down by the addition of water to the solution in nitric acid; it is mixed with binitrosulphobenzide. Hot alcohol leaves the latter undissolved in the form of a white crystalline powder. On cooling, the alcoholic solution deposits the nitrosulphobenzide in the form of a honey-yellow, ductile mass, which solidifies in the cold and fuses at 194° to 198° F. This body is insoluble in cold water, but dissolves a little in hot water; it separates from this solution in yellow oil-drops.

Amidosulphobenzide, $C^{24} H^9 (NH^2) S^2 O^4$.—The alcoholic solution of nitrosulphobenzide is treated with sulphuret of ammonium; sulphur is deposited. The solution is acidified with muriatic acid and precipitated with potash. The yellowish precipitate is repeatedly dissolved in muriatic acid and precipitated with potash; when suffi-

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ciently purified, it forms a precipitate consisting of microscopic four-sided prisms.

This body is difficult of solution in cold water, but dissolves readily in hot water and in alcohol. On platinum foil it burns with a strongly sooty flame.

The Compound of this Body with Muriatic Acid, $C^{24} H^9 (NH^2) S^2 O^4$, HCl, forms reddish, four-sided prisms; it is readily soluble in water, and the solution is red. It fuses at 194° F., and solidifies in a gum-like form.

The Compound with Chloride of Platinum, $C^{24} H^9 (NH^2) S^2 O^4$, $HCl + PtCl^2$, forms microscopic crystals, and is insoluble in cold water; it is partially decomposed by water, and dissolves even in cold alcohol.

Binitrosulphobenzide, $C^{24} H^8 (NO^4)^2 S^2 O^4$.—By continued treatment with fuming nitric acid, or a mixture of this acid with sulphuric acid, sulphobenzide is converted into binitrosulphobenzide.

This body forms small, white, silky, rhombic prisms, and is insoluble in water. It is but slightly soluble in alcohol and æther even with the assistance of heat. It fuses at 327° F., solidifies afterwards in a radiate crystalline form, and sublimes without decomposition at 518° F.

By treatment with sulphuret of ammonium, binitrosulphobenzide furnishes binamidosulphobenzide, $C^{24} H^8 (NH^2)^2 S^2 O^4$. The muriate of this body, $C^{24} H^8 (NH^2)^2 S^2 O^4 + 2HCl$, crystallizes in elongated, four-sided, rhombic prisms, of a reddish colour. It is readily soluble in water and alcohol, and is not decomposed at 212° F. From the solution of the latter compound, perchloride of platinum throws down the double salt $C^{24} H^8 (NH^2)^2 S^2 O^4 + 2HCl + PtCl^2$.

Amidosulphobenzide and binamidosulphobenzide furnish no definite products of substitution with iodide of æthyle, but only greasy, non-crystallizable substances.

Bichloride of Sulphobenzide, $C^{24} H^8 Cl^2 S^2 O^4$, 2HCl, is obtained by passing chlorine over fused sulphobenzide, when it distils over in yellow drops. It is soluble in alcohol and æther, insoluble in water; it is heavier than water, attracts water from the air, and evaporates readily. It distils without decomposition at 302° F., and burns with a smoky flame. Dilute alkalies neither dissolve nor decompose it. If it be quickly heated, it becomes converted into muriatic acid and

Bichlorosulphobenzide, $C^{24} H^8 Cl^2 S^2 O^4$, which is deposited in the neck of the retort in a yellow crystalline form. This body is also produced by the treatment of the protochloride of sulphobenzide with alcoholic solution of potash; chloride of potassium is separated.

This body is quite insoluble in water, and appears under the microscope to form long lanceolate crystals. It fuses at about 306° F., solidifies in a crystalline form, and sublimes far below its melting-point. By frequently repeated fusion and cooling, the melting-point sinks to 150° F. It is insoluble in alkalies; alcoholic solution of potash decomposes it during distillation, when a portion passes undecomposed together with pure sulphobenzide. Zinc and

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sulphuric acid do not regenerate the sulphobenzide from this compound.

From the preceding investigation the author concludes that the formula of sulphobenzide is $C^{24}H^{10}S^2O^4$, and not $C^{12}H^5SO^2$. The rational formulæ of the compounds described are—

$$\left.\begin{matrix} C^{12}H^4(NO^4)SO^2 \\ C^{12}H^5 \quad\quad SO^2 \end{matrix}\right\} = \text{nitrosulphobenzide.}$$

$$\left.\begin{matrix} C^{12}H^4(NO^4)SO^2 \\ C^{12}H^4(NO^4)SO^2 \end{matrix}\right\} = \text{binitrosulphobenzide.}$$

$$\left.\begin{matrix} C^{12}H^4(NH^2)SO^2 \\ C^{12}H^5 \quad\quad SO^2 \end{matrix}\right\} = \text{amidosulphobenzide.}$$

$$\left.\begin{matrix} C^{12}H^4(NH^2)SO^2 \\ C^{12}H^4(NH^2)SO^2 \end{matrix}\right\} = \text{binamidosulphobenzide.}$$

$$\left.\begin{matrix} C^{12}H^4(Cl)SO^2 \\ C^{12}H^4(Cl)SO^2 \end{matrix}\right\} 2HCl = \text{bichloride of sulphobenzide.}$$

$$\left.\begin{matrix} C^{12}H^4(Cl)SO^2 \\ C^{12}H^4(Cl)SO^2 \end{matrix}\right\} = \text{bichlorosulphobenzide.}$$

The Salts of Sulphophenylic Acid with sodium, calcium, barium, zinc, lead and copper, are all readily soluble in water and alcohol, and crystallize in microscopic rhombic laminæ. By heating sulphophenylate of lead with iodide of æthyle to 212° F. in a sealed tube, sulphophenylic æther is formed, which shoots out into fine needles when the alcoholic solution is evaporated over sulphuric acid. These needles are readily soluble in water, but less so in alcohol; they are not volatile, and when heated with potash furnish alcohol and sulphophenylate of potash; the same decomposition into alcohol and sulphophenylic acid takes place even during the rapid evaporation of the aqueous solution.

Sulphophenylate of Aniline crystallizes in long silky needles, grouped in a radiate form; they are usually of a somewhat reddish colour, and dissolve readily in water and alcohol, but are scarcely soluble in æther; they fuse at 394° F., solidify into a radiate-crystalline mass, and sublime, forming colourless crystals, even below their melting-point.

Sulphophenylanilide, which has already been described by Biffi, is formed, with evolution of heat, by the action of aniline upon protochloride of sulphophenyle; it separates from the alcoholic solution in colourless quadrangular pyramids. These are readily soluble in æther, but slightly so in water; from the latter they crystallize in fine white needles, composed of many small pyramids; they fuse at about 221° F., and solidify only after some time to form a nearly glassy mass. In water they fuse even below 212° F. Sulphophenylanilide is isomeric with amidosulphobenzide.

Sulphobenzide appears to be analogous to sulphonaphthaline, $\left.\begin{matrix} C^{20}H^7SO^2 \\ C^{20}H^7SO^2 \end{matrix}\right\}$. Sulphonaphthaline is crystalline, and fuses between 194° and 203° F., forming a yellowish-brown mass, which solidifies on cooling in a gum-like form; it becomes blackened at a higher

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temperature, and only a portion sublimes unchanged. It does not dissolve in water, and scarcely in cold alcohol, but rather more in hot alcohol. It is decomposed by fuming nitric acid, and water precipitates white flakes from the solution. It is not decomposed by alcoholic solution of potash at a high temperature, any more than sulphobenzide.—Liebig's *Annalen*, c. p. 207.

On the Action of Succinic and Citric Acids upon Glycerine. *By* Dr. J. M. van Bemmelen.

The investigations of Berthelot have shown that glycerine may be combined with several monobasic acids. If in grouping the compounds obtained we proceed according to Gerhardt's views, we must regard them, as Limpricht has already done, as glycerine, in which 1, 2, or 3 equivs. of hydrogen are displaced by the same number of the radicals of the organic acids. In this way monostearine, distearine, and tristearine will have the following formulæ:—

Monostearine.	Distearine.	Tristearine.
$C^6\ H^5\ O^2$	$C^6\ H^5\ O^2$	$C^6\ H^5\ O^2$
H	H	$C^{36}\ H^{35}\ O^2$
H	$C^{36}\ H^{35}\ O^2$	$C^{36}\ H^{35}\ O^2$
$C^{36}\ H^{35}\ O^2$	$C^{36}\ H^{35}\ O^2$	$C^{36}\ H^{35}\ O^2$
O^4	O^4	O^4.

The author's object in the following investigation was to test the correctness of such a supposition, by endeavouring to prepare compounds with bibasic and tribasic acids, by which H^2 and H^3 must be displaced in glycerine. The compounds which the author has prepared and investigated at the instigation of Prof. J. van Kerckhoff, are *succinine* and *citrine*.

Succinine, $C^{14}\ H^{10}\ O^{10}$.—Equal parts of succinic acid and glycerine are fused together in a retort at 266° F. Water is driven off, and a syrup is obtained which is soluble in water and alcohol, but insoluble in æther,—an unstable compound of the two bodies, if indeed any combination took place. When the syrup was then further heated to 392°–428° F., water was continually evolved, and there remained a hard mass, which no longer had an acid taste. It was blackish-brown; colourless in thin strata.

This mass is insoluble in water, alcohol, æther, and sulphuret of carbon. When it is left for a long time in contact with alkalies, it dissolves entirely; this takes place more rapidly with the aid of heat.

When it is boiled with water and alcohol, it dissolves very gradually with decomposition. The colourless solutions, when evaporated, leave a nearly colourless syrup, which is capable when heated of furnishing the same substance from which it was produced.

That succinic acid and glycerine were again formed by the reception of water when this substance was dissolved, was proved by decomposition with the aid of oxide of lead. Thus when it was boiled for some time in water with an excess of oxide of lead, decomposition gradually occurred, by which the body was completely decomposed into succinic acid and glycerine. The analysis is—

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C	48·30	48·52	48·52	14	48·28
H	5·91	5·75	5·72	10	5·75
O	45·79	45·73	45·76	10	45·97

The formula $C^{14} H^{10} O^{10}$ only differs from the sum of succinic acid and glycerine by 4 equivs. of water. We have thus—

$$\left.\begin{matrix} C^6 H^5 O^2 \\ H \\ H \\ H \end{matrix}\right\} O^4 + \left.\begin{matrix} C^8 H^4 O^4 \\ H^2 \end{matrix}\right\} O^4 = \left.\begin{matrix} C^6 H^5 O^2 \\ H \\ C^8 H^4 O^4 \end{matrix}\right\} O^4 + \left.\begin{matrix} H^2 \\ H^2 \end{matrix}\right\} O^4,$$

and therefore two of the three displaceable equivalents of hydrogen in the glycerine are replaced by the one bibasic radical of the succinic acid.

Benzosuccinine, $\left.\begin{matrix} C^6 H^5 O^2 \\ C^{14} H^5 O^2 \\ C^8 H^4 O^4 \end{matrix}\right\} O^4$.—1 equiv. of succinic acid, 1 equiv. of benzoic acid, and more than 1 equiv. of glycerine are heated in a retort. At 284° F. water passes, and the temperature is then raised to 392° F. A thickly-fluid black mass is obtained in the retort; this, on cooling, solidifies into a tough elastic substance, and may then be drawn out into threads.

It was insoluble in æther, alcohol and water. By boiling with water it was slowly decomposed. When it was boiled with alcohol, the latter became turbid, but again grew clear by standing, and the brown substance settled. At the same time it is again slowly decomposed, for the water and alcohol, which however were quite colourless, left a thick syrup on evaporation, like that of succinine, from which, by a further application of heat, benzoic acid was volatilized.

If the substance be boiled with muriatic acid, it fuses, and floats upon the surface of the fluid like a thick oil-drop. It is, however, soon dissolved with decomposition. In concentrated sulphuric acid it is immediately dissolved with the aid of heat; the fluid becomes dark brown.

By boiling with caustic potash, the substance dissolves pretty rapidly, forming a brown fluid. From this muriatic acid precipitates benzoic acid. In the fluid filtered from this, chloride of barium produces a white precipitate after the addition of ammonia and alcohol. This property belongs to succinic acid, which is distinguished thereby from benzoic acid. If the substance be heated with anhydrous phosphoric acid, a very strong odour of acroleine is evolved. The substance employed for analysis is extracted with water and alcohol, and then heated again to 392° F.

The substance is but slowly converted into benzosuccinine, because benzoic acid does not easily enter into the combination; the author therefore treated it twice successively with benzoic acid, and obtained benzosuccinine. The analyses are as follows:—I. of the substance above described; II. of a product in which benzoic acid was employed in great excess; and III. of the same product as II.

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after it had been a second time heated with benzoic acid. The third substance alone has the exact composition of benzosuccinine.

	I.	II.	III.		
C	57·27	59·48	60·71	28	60·43
H	5·42	5·11	5·11	14	5·03
O	37·31	35·41	34·18	12	34·53

Citrine.—1 equiv. of crystallized citric acid is heated with an excess of glycerine in a retort. The mass fuses at 212° F., and when it has been kept at 320° to 338° F. until no more water is driven off, it forms a syrup, which afterwards becomes hard and tough, yellowish-brown and porous. At 392° F. it had the same consistence as at the ordinary temperature. The fine powder was white. It gradually became softer in the air. It did not dissolve in water, alcohol and æther. When left for a long time in contact with cold water, it communicated no acid reaction to it. When boiled with water and alcohol, these leave a thick acid syrup, which again becomes solid on cooling; this substance therefore is also slowly decomposed in this way.

The coarse powder was extracted for a short time with alcohol, then washed, quickly dried, and again heated to 336° F. in a current of dry air. The analysis of this body gave—

C	44·51	24	44·71
H	5·41	18	5·59
O	50·08	10	49·70

This body is consequently *citrodiglycerine*, produced from glycerine and citric acid in the following manner:—

$$2\left\{\begin{matrix}C^6\,H^5\,O^2\\H^3\end{matrix}\right\}O^4\Big\} + \left.\begin{matrix}C^{12}\,H^5\,O^8\\H^3\end{matrix}\right\}O^6 = \left.\begin{matrix}C^6\,H^5\,O^2\\H^3\\C^6\,H^5\,O^2\\C^{12}\,H^5\,O^8\end{matrix}\right\}O^4 + \left.\begin{matrix}H^3\\H^3\end{matrix}\right\}O^6.$$

Potash saponifies this body, forming glycerine and citrate of potash.

Citromonoglycerine was obtained by the author by heating glycerine containing 6 per cent. of water and of spec. grav. 1·23 (which before its employment had been heated for an hour to 266° F.) with an equal equivalent of citric acid, gradually raising the temperature to 320° F.

A remarkably hard, light yellow, transparent mass was obtained; it attached itself firmly to the glass, and could not be separated from it. It was only distinguished from citrodiglycerine by its much greater hardness and its lighter colour.

In the air it underwent no change, and did not even become softer. In water it remained undissolved, and gave it no acid reaction. By boiling, only a very small quantity of it was dissolved, even in a quarter of an hour. Muriatic acid soon dissolves it with the aid of heat, and concentrated sulphuric acid immediately, whilst the fluid becomes blackish.

Citric acid and glycerine were obtained from it in the same way

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as from citrodiglycerine by treatment with potash and oxide of lead. All the same reactions were obtained. Analyses:—

	I.	II.	III.	IV.		
C	44·35	44·72	47·68	46·64	18	46·96
H	4·30	4·60	4·73	3·58	10	4·34
O	51·35	50·68	47·69	48·78	14	48·71

Thus it appears that a tribasic acid (citric acid) and a bibasic acid (succinic acid) have a very different action upon glycerine from that of the monobasic acids, the volatile fatty acids. The latter only combine with glycerine after long contact, without the occurrence for a moment of any mutual dissolution. The compounds are soluble in alcohol and æther. In the two former, on the contrary, a dissolution occurred at 212° to 248° F.; a syrup is produced and water expelled. If the heat be carried to 302°–392° F. in a retort, the syrup becomes thicker and thicker, until in a short time, when 4 and 6 equivs. of water are driven off, a solid and perfectly neutral substance has been formed, which does not dissolve in water, alcohol or æther. By digestion with water and alcohol, however, especially at a boiling heat, it is gradually dissolved with decomposition, the acid and glycerine being reproduced by the assimilation of water.—*Journ. für Prakt. Chem.*, lxviii. p. 84.

On the Production of Mannite by Marine Plants.

By T. L. Phipson.

When some marine Algæ are dried in the open air, they produce an efflorescence of mannite on their surface. Such are the *Laminaria saccharina, L. digitata, Rhodymenia palmata, Fucus siliquosus, F. nodosus, F. vesiculosus, F. saccharinus, F. serratus*, &c. The author has observed this production of mannite on many of these Algæ, and feels no doubt that all the Algæ which contain vegetable mucilage may give origin to this substance when placed in circumstances favourable to its production.

It has been supposed that the production of mannite by these plants was due to a *secretion* by the living plant; the author has ascertained that it is only produced after the cessation of the vital activity of the plant. He also thinks that the production of mannite is always the result of a peculiar fermentation, the effect of which is to deoxidize the vegetable mucilage and convert it into mannite.

Many marine Algæ contain such large quantities of mucilage, that some naturalists have endeavoured to make use of this product in the arts. (Thus Brown (Edin. Phil. Journ., xxvi. p. 409) found that by prolonged ebullition with dilute sulphuric acid, this mucilage was converted into *arabine*.)

The author obtained considerable quantities of mannite by placing the sea-weeds, whilst moist, between sheets of brown paper, so that the access of air was not prevented, and leaving them thus for about eight days. Their surface was then covered by an efflorescence of

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mannite. In this case it is produced rather in a granular than a crystalline form; but when dissolved in water, it crystallizes on the evaporation of the liquid in tufts of long colourless needles.

The production of the mannite may take place as follows. Supposing the formula of the mucilage to be $C^{12} H^{10} O^{10}$, which represents the composition of the substance dried *in vacuo* at 266° F., by losing 1 equiv. of oxygen in the presence of water it may split into 2 equivs. of mannite; thus—

$$C^{12} H^{10} O^{10} + 4HO = 2C^6 H^7 O^6 + O$$

Vegetable mucilage + water = mannite +oxygen.

Mannite is also produced during the viscous fermentation, in which a viscous matter of the nature of gum is formed (in wines, beers, and vegetable juices in course of alteration), and in this case the mannite is evidently produced by a deoxidizing action exerted by the fermenting matter upon the viscous substance.

The intercellular mucilage of a sea-weed being decomposed during the production of mannite, the superficial tissue of the plant is deteriorated; this is the case especially in the *Laminaria saccharina*, one of the Algæ which furnishes most mannite. With the microscope the latter is seen accompanied by a great number of isolated spherical cells, arising from the destruction of the tissues of the plant; the application of water dissolves the mannite and sets free the cells. In the frond, when there is no mannite on its surface, these cells are seen in juxtaposition and implanted in a mucilage, forming a smooth continuous layer, which becomes pulverulent by the formation of the mannite.

The body which causes the alteration of the mucilage in the Algæ is probably the albuminous matter which is contained in all vegetables, and becomes altered in the air, giving rise by its continued alteration to those disagreeable odours which characterize the putrefaction of the Algæ.

The author therefore thinks that mannite is produced rather from vegetable mucilage than from sugar, and that wherever vegetable mucilage is subjected to a deoxidizing action, mannite will be formed. —*Comptes Rendus*, Dec. 1, 1856, p. 1056.

Notes upon Sulphomesitylic Acid. *By* Dr. H. Hlasiwetz.

By mixing acetone with fuming sulphuric acid, diluting the mixture with water, and saturating it with lime or baryta, Kane obtained salts of a conjugate acid, which he called sulphomesitylic acid. Like all the conjugate acids, it is very unstable, and can only be investigated in its salts.

The author had on a former occasion endeavoured to obtain a sulphur compound by the decomposition of the lime-salt with sulphuret of potassium.

In his text-book of chemistry, Gerhardt observes that he had endeavoured unsuccessfully to prepare this acid or its salts, and that it is possible that under the circumstances acetone only furnishes some sulphomethylic acid.

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This statement determined the author to repeat the experiment; for if Kane's salt has no existence, and instead of it only sulphomethylate of lime is produced, the sulphuretted product of decomposition formerly obtained can only have been sulphuret of methyle.

The following mixtures were investigated as to their containing the acid in question:—

a. 150 grms. of acetone mixed with 300 grms. of sulphuric acid (first hydrate), and left standing for twenty-four hours, then diluted with water, saturated with powdered marble, &c.

b. 60 grms. of acetone and 30 grms. of sulphuric acid (first hydrate), treated in the same way as *a.*

c. 60 cub. centims. of acetone and 60 cub. centims. of sulphuric acid, mixed without external cooling; in a short time the mixture became so much heated that it was obliged to be cooled. The mass had become quite black, and evolved sulphurous acid, which was not previously (*a* and *b*) observed. On dilution, a thick black tar separated, whilst in *a* and *b* a stratum of oxide of mesityle floated on the surface, and was removed before saturation.

d. 60 cub. centims. of acetone and 30 cub. centims. of sulphuric acid, mixed with refrigeration, and diluted and saturated after one hour. The dilute fluid was pale reddish-yellow, and yielded very little oxide of mesityle. (However, fresh quantities of this ætherial substance were constantly separated during the saturation with lime, and the largest quantity was obtained by the distillation of the fluid. But then the residue of the distillation scarcely gave any sulphomesitylates.)

e. 60 cub. centims. of acetone mixed with 30 cub. centims. of oil of vitriol, with refrigeration. Further treated after three hours.

f. 60 cub. centims. of acetone, mixed as before with 120 cub. centims. of strong fuming sulphuric acid. Diluted and saturated after twelve hours. The separation of oxide of mesityle in *e* and *f*, smaller in quantity and more coloured than with hydrated sulphuric acid.

All these acid mixtures were then treated in the same manner. The thick paste of sulphate of lime obtained after neutralization with marble was pressed, and the mass again stirred up with water and pressed. The united filtered fluids were then evaporated at a very gentle heat. On cooling, a further portion of sulphate of lime always separated in crystals; the fluid filtered from these was then left to evaporate spontaneously until it had become as thick as a syrup. Of the honey-yellow mother-liquors thus obtained, some (*b*, *e*, *f*) became filled with small crystals; others (*a*, *d*) only dried into a gum-like mass. The result in all cases was small. The crystals (prisms) could hardly be separated from the mother-liquor which caused them to stick together.

All these residues, the crystalline ones as well as those which were merely dried (which no doubt would also have crystallized if their quantity had been larger), contain the peculiar lime-compound to which Kane has called attention. They dissolve completely in hot alcohol, leaving behind a trace of sulphate of lime. This solution, when concentrated and cooled, sets into a jelly, and the salt is

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precipitated by æther. By this means a gelatinous paste is produced, which was freed from the fluid by pressure between linen, and repeatedly washed with æther. The mass obtained is uncrystalline, and dries into a gum-like mass under the air-pump. When triturated, it is a white or slightly yellowish powder. This, when heated, evolves an aromatic penetrating odour, becomes black, and finally leaves sulphate of lime.

The aqueous solution, acidulated with nitric acid and mixed with chloride of barium, furnishes an abundant precipitate of sulphate of baryta. Concentrated sulphuric acid, with the assistance of heat, dissolves the substance without perceptible change. As has been observed, the amount is always small; the quantity is largest in proportion with the long action of hydrated sulphuric acid (*a*, *b*), or by the employment of fuming sulphuric acid (*f*).

The analytical results are not concordant, which is to be attributed to an imperfect purification of the material. This, however, is very difficult. The substance was dried under the air-pump, and then at 212° F. Analysis gave—

					Kane obtained.
Carbon	28·7	27·8	..	..	30·3
Hydrogen	4·1	4·0	..	..	4·4
Lime	20·3	21·3	22·0	22·7	23·7

These analyses, as well as the whole behaviour of the compound, prove that it is not sulphomethylate of lime. Kane deduces from his numbers the formula $(CaO, SO^3) + C^6 H^5 O$, which is not probable, being destitute of analogy, as already observed by Gmelin and Gerhardt, although it agrees with the analysis. But if we take into consideration the mode of production of this body, it may perhaps be conceived in a different way.

It is certainly no acetone compound, but a compound of the so-called oxide of mesityle. It is also most abundantly produced by the employment of pure oxide of mesityle and sulphuric acid. But under these circumstances the alcohols and æthers not only form conjugate sulphuric acids, but also compounds with $S^2 O^4$.

In exactly the same manner, hydrated oxide of phenyle furnishes the so-called sulphobenzidic acid (Mitscherlich), $\left.\begin{matrix} C^{12} H^5 O \\ H\ O \end{matrix}\right\} S^2 O^4$ or $\left.\begin{matrix} C^{12} H^5 S^2 O^4, O \\ HO \end{matrix}\right\}$ (Gerhardt), only to mention one of the many examples. This compound may therefore probably be one of the same kind, and the lime-salt may have the formula $\left.\begin{matrix} C^6 H^5 O \\ CaO \end{matrix}\right\} S^2 O^4$. This formula requires—

C	25·5
H	3·5
O	5·9
CaO	19·8
$S^2 O^4$	45·3

which certainly only approaches the quantities found; but at the same time it must be remembered that the preparations could not be obtained pure.

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Kane states that the baryta-salt of his sulphomesitylic acid, when decomposed by sulphuric acid, furnishes a fluid which smells strongly of mesitic æther, contains sulphovinic acid, and becomes decomposed when evaporated, evolving sulphurous acid. The author has never obtained a salt of persulphomesitylic acid (Kane). The lime-salt is described as consisting of granules and little columns; it is said to have the formula $2(CaO, SO^3) + C^6 H^6 O^2$. It is not impossible that it was the preceding salt contaminated with sulphate of lime. The same compounds which are furnished by acetone with sulphuric acid are also obtained, and indeed in greater abundance, with oxide of mesityle itself. This was mixed with an equal volume of oil of vitriol, and the thick brown fluid was diluted with water after standing for twenty-four hours. No more oxide of mesityle separated, and on neutralization with lime as much lime-salt was obtained from 1 part of oxide of mesityle as from five times the quantity of acetone. It was however impossible to obtain the salt, which was diffused in the mother-liquor in the form of small deliquescent crystals, in a state fit for analysis; the author therefore endeavoured to combine the acid with another base.

Copper-salt.—The aqueous solution of the lime-salt was mixed with solution of sulphate of copper as long as sulphate of lime was thrown down; the fluid was filtered from this and evaporated at a gentle heat. There remained a dark green residue, which was exhausted with boiling alcohol. The filtered concentrated green solution, after standing for some time, gave a considerable quantity of voluminous, greenish, small acicular crystals. The mother-liquors furnished another portion, and on spontaneous evaporation left a crystalline paste, which could only be freed from the mother-liquors with difficulty.

The crystals, when pressed, are light green, and cover the paper with a satin-like film. They are readily soluble in water and in alcohol if not too strong; when heated, they evolve sulphurous acid and the odour of oxide of mesityle. Dried at 212° F., they become grayish-green. The analysis gave—

	In 100 parts.
Carbon	21·7
Hydrogen	4·2
Oxide of copper.....	23·0

The formula $\left.\begin{matrix} C^6 H^5 O \\ CuO \end{matrix}\right\} S^2 O^4 + 2Aq$ requires C 21·1, H 4·1 and CuO 23·2.

Ammonia-salt.—If the lime-salt be decomposed by carbonate of ammonia, the carbonate of lime separated by filtration, the fluid evaporated, and the residue extracted with strong alcohol, a butyraceous, deliquescent, crystalline mass is left by spontaneous evaporation. When heated with potash, it is decomposed into ammonia, and oxide of mesityle which distils over. Certainly no sulphomethylic acid is formed; the author, on the contrary, observed the constant formation of salts of a peculiar conjugate acid.

The analyses of these salts cannot well be brought to agree with such compounds of sulphuric acid; whilst from their mode of pro-

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duction, properties and behaviour, they may be regarded as conjugate compounds of sulphurous acid. The composition of the copper-salt appears to confirm this view.

Oxide of mesityle, $C^{18} H^{10} O^2$, is a compound which has not yet found its place in the system. We are equally unacquainted with the exact constitution of some other derivatives of acetone, such as the pteleyle compounds, mesitylene, &c.

Perhaps the following remarks upon these bodies are admissible. It is at present supposed that the alcohols, æthers, acids, and their derivatives, are derived chiefly from two kinds of radicals,—an electro-positive one, consisting only of C and H; and an electro-negative one, which also contains O. For one of the best known series the terminal members are, methyle, $C^2 H^3$, and formyle, $C^2 H$. These radicals combine with oxygen (oxides, æthers, and anhydrous acids), with oxygen and water (hydrated oxides, alcohols, and hydrated acids), or with hydrogen alone (hydrurets, aldehydes). But besides these general compounds, there is a homologous series of hydrocarbons, $n(C^n H^n)$, which from their mode of production approach immediately to the alcohols, $C^2 H^2$, $C^4 H^4$, $C^6 H^6$, $C^8 H^8$ ...

Now these hydrocarbons cannot be derived from the homologous radicals of the alcohols and æthers; they must therefore be either radicals or compounds of radicals. We have valid reasons for asserting the latter; it is too well known that everything is in favour of the radical nature of the residue $C^n H^{n-1}$, to need its repetition here. Thus for every family we attain the triads of radicals:—

$C^n H^{n-1}$.	$C^n H^{n-1} O^2$.	$C^n H^{n+1}$.
$C^2 H$	$C^2 HO^2$	$C^2 H^3$
Formyle.	Formoxyle.	Methyle.
$C^4 H^3$	$C^4 H^3 O^2$	$C^4 H^5$
Vinyle.	Acetoxyle.	Æthyle.
$C^6 H^5$	$C^6 H^5 O^2$	$C^6 H^7$
Allyle.	Propyoxyle.	Propyle.
&c.	&c.	&c.

(By the consistent carrying out of the theory of substitution, we shall probably be obliged to regard the oxygenated radicals as substituted and secondary, for example, $C^2 \left\{ \begin{matrix} H \\ H \\ H \end{matrix} \right.$ = methyle, $C^2 \left\{ \begin{matrix} H \\ O \\ O \end{matrix} \right.$ = formoxyle, &c., since the same function must be attributed to oxygen under certain circumstances, as has long been established beyond a doubt with regard to Cl, Br, I, to which it is most nearly allied in its nature. Thus we have only $(C^n H^{n-1})$ and $(C^n H^{n+1})$ as type radicals.)

To the mode of combination of the radicals $(C^n H^{n-1})$ the same applies as to those of the general formula $(C^n H^{n+1})$, that is to say, they give neutral oxides and hydrated oxides, æthers and alcohols; they take the place of H in ammonium, &c. The most numerous proofs are furnished by the allyle group; we have moreover the base

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$\left.\begin{matrix} C^4 H^3 \\ H \\ H \\ H \end{matrix}\right\}$ NO, discovered by Natanson, and likewise the compounds of the parallel radicals phenyle, thymyle, &c. Future investigations will no doubt make us acquainted with a number of the æthers, alcohols, amines, &c. still to be derived from these radicals.

Secondary radicals must be formed from the above-mentioned radicals, as we admit with certainty to be the case with other radicals. It is then the same as if we considered acetoxyle, $C^4 H^3 O^2$, as substituted formoxyle $= C^2(C^2 H^3)O^2$, æthyle, $C^4 H^5$, as substituted methyle $= C^2 \left(\begin{matrix} C^2 H^3 \\ H \\ H \end{matrix}\right)$, benzoxyle as substituted formoxyle $= C^2(C^{12} H^5)O^2$, &c. It is therefore extremely probable that there is also a substituted vinyle, for example, $C^4 \left(\begin{matrix} C^2 H^3 \\ H \\ H \end{matrix}\right) = C^6 H^3$, which is isomeric with allyle. (Allyle is perhaps a substituted $C^2 H$, in which H is replaced by $C^4 H^5$.) This substituted vinyle is perhaps the radical of oxide of mesityle, which might be its æther:—

$$\left.\begin{matrix} C^4 \left(\begin{matrix} C^2 H^3 \\ H \\ H \end{matrix}\right) O \\ C^4 \left(\begin{matrix} C^2 H^3 \\ H \\ H \end{matrix}\right) O \end{matrix}\right\} = C^{12} H^{10} O^2.$$

This view gains in probability if we take into consideration its production from acetone, the basis of which is a substituted acetyle:—

$$2\left\{\begin{matrix} C^4 \left(\begin{matrix} C^2 H^3 \\ H \\ H \end{matrix}\right) O^2 \\ H \end{matrix}\right\} - H^2 O^2 = \left.\begin{matrix} C^4 \left(\begin{matrix} C^2 H^3 \\ H \\ H \end{matrix}\right) O \\ C^4 \left(\begin{matrix} C^2 H^3 \\ H \\ H \end{matrix}\right) O \end{matrix}\right\}.$$

Acetone. Oxide of mesityle.

The action of the sulphuric acid therefore consists principally in an abstraction of water. (The author is engaged in trying whether the æther $\left.\begin{matrix} C^4 H^3 O \\ C^4 H^3 O \end{matrix}\right\}$ may be prepared in the same way from the ordinary acetaldehyde.)

Under this conception the chloride and sulphuret of mesityle $= C^4 \left(\begin{matrix} C^2 H^3 \\ H \\ H \end{matrix}\right)$ Cl, and $C^4 \left(\begin{matrix} C^2 H^3 \\ H \\ H \end{matrix}\right)$ S also naturally fall.

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If we thus allow the faculty of substitution of the hydrogen of the radicals $C^n H^{n-1}$ to prevail throughout, it would be possible also that we may likewise derive the following compounds from the radical $C^2 H$:—

$\left.\begin{matrix} C^2 H \\ C^2 H \end{matrix}\right\}$, formyle.

$\left.\begin{matrix} C^2 H \\ H \end{matrix}\right\}$, methylene.

$\left.\begin{matrix} C^2 H \\ Cl \end{matrix}\right\}$, chloride of methylase (Laurent).

$\left.\begin{matrix} C^2 Br \\ Br \end{matrix}\right\}$, bromide of carbon (Löwig)?.

$\left.\begin{matrix} C^2(C^4 H^3) \\ H \end{matrix}\right\}$, mesitylene (Kane); $\left(\begin{matrix} C^2 C^4 H^3 \\ H \end{matrix}\right)3$ according to Hofmann.

$\left.\begin{matrix} C^2(C^4 H^3) \\ Cl \end{matrix}\right\}$, chloride of pteleyle (Kane).

$\left.\begin{matrix} C^2(C^4 H^3) \\ I \end{matrix}\right\}$, iodide of pteleyle (Kane).

$\left.\begin{matrix} C^2(C^4 H^3) \\ NO^4 \end{matrix}\right\}$, nitropteleyle?.

$\left.\begin{matrix} C^2(C^4 H^3).O \\ HO \end{matrix}\right\}$, mesitaldehyde (Kane; perhaps the alcohol of this series?).

Vinyle, $C^4 H^3$, might even be a $C^2 H$ substituted by methyle $=C^2(C^2 H^3)$, just as acetyle, $C^4 H^3 O^2$, is a substituted formoxyle $=C^2(C^2 H^3)O^2$.

Methole (Weidmann and Schweizer) is isomeric with vinyle. The isomerism probably consists in its being a substituted methyle $=C^2\left(\begin{matrix} C^2 H \\ H \\ H \end{matrix}\right)$.

It is very probable that the above-mentioned radicals also occur by substitution in acid radicals, as for example in the radical of acroleine and acrylic acid, which may be formulized in the most perfect agreement with the products of the decomposition of these compounds:—

$\left.\begin{matrix} C^2 (C^4 H^3) O^2 \\ H \end{matrix}\right\}$, hydruret of acryle, corresponding to $\left.\begin{matrix} C^2 (C^4 H^3) O^2 \\ H \end{matrix}\right\}$, hydruret of propioxyle, and $\left.\begin{matrix} C^2 (C^4 H^3) O^2.O \\ HO \end{matrix}\right\}$, acrylic acid, corresponding to $\left.\begin{matrix} C^2 (C^4 H^5) O^2.O \\ HO \end{matrix}\right\}$ propionic acid; and in the same way all the homologues of the general formula $(C^n H^{n-2} O^4)$, such as damaluric acid, moringic acid, phocænic acid, erucic acid, &c. (Rochleder).—*Sitzungsber. der Akad. der Wiss. zu Wien*, 1856.

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CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Note on the Intimate Composition of Leather. By M. PAYEN.

THE author's analyses, made with the assistance of M. Billequin, have confirmed his previous results, and shown that in the skins of oxen, treated by the usual processes of tanning, and kept in contact with solutions of tannin from oak-bark, or in tan-pits, for eight or twelve months up to seven years, there remains an excess of tannin, which may be extracted with pure water by the solution of a portion of the combination formed by it with the less aggregated substance of the skin*.

The quantity of soluble matter thus obtained from leather which had remained seven years in the pits, formed 6·469 per cent. of the weight of the tanned skin, and gave only 1·548 per cent. of nitrogen.

From a well-tanned skin, 8·09 of soluble matter, containing 2·8 per cent. of nitrogen, were obtained; an ordinary Parisian leather gave 7·37 of soluble matter containing 3·98 per cent. of nitrogen. In these latter samples, therefore, the excess of tannin appeared to be less, and the quantity of nitrogenous matter extracted by water greater than in the first, or in proportion to the duration of the tanning.

In the three samples, the *fibrous* portion of the skin which resisted the action of water and ammonia was 58·88 per cent. (average of two analyses 58·76 and 59) in the leather of seven years, and 46·60 and 48·80 per cent. in the two others. These quantities, which are in direct proportion to the duration of the tanning, appeared to depend upon a gradual loss of the less aggregated portion of the skin, which is capable of forming with the tannin of the oak a compound soluble in ammonia.

The determination of the nitrogen, to show the proportions of tannin combined in the persistent substance of the three origins, gave the following results in hundredths:—

	I.	II.	III.
Nitrogen	13·272	12·235	13·59
Ash	0·733	0·660	0·606

The differences are slight, and have no relation to the duration of the tanning; it would appear that the saturation of the persistent matter by the tannin takes place long before the period usually assigned for tanning. It is the proportion of the fibrous substance, and not its degree of tanning, that causes a difference between these products, and probably an actual superiority in that in which it predominates.

After determining this persistent portion and the nitrogen of the entire skin, the difference gives the proportion of the soluble part extracted by ammonia and its amount of nitrogen; thus—

* The preliminary operations of the tanning having extracted the hairs and nearly all the fatty matter, the author, in order to render the composition still less complex, removed with the epidermis a layer of the subjacent tissue, so that the greater part of the hair-follicles and the sudoriferous canals were got rid of, and the remainder of the skin corresponded with the parts which are almost entirely convertible into gelatine before the operation of tanning.

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	I.	II.	III.
Persistent fibrous substance.....	58·88	46·60	48·80
Soluble matter	41·12	53·40	51·20

If the matter dissolved by ammonia were not altered during solution and evaporation, it ought to be found entirely in the dried residue; this was not the case, as experiment gave:—

	I.	II.	III.
Instead of	41·12	53·40	51·20
	18·46	29·77	28·75
Difference or loss	22·66	23·63	22·45

This loss must be a consequence of the instability of the elements of the dissolved matter, rendering them liable to be evolved in the form of ammoniacal compounds under the influence of water, ammonia and heat.

The determination of the nitrogen of these residues gave the following quantities in hundredths:—

I.	II.	III.
5·112	6·006	7·151

The loss of nitrogen therefore corresponded with the loss of weight. To determine this loss, it was necessary to ascertain the amount of nitrogen in the skin, to deduct from this the amount contained in the *fibrous* portion, and to calculate thus what the dissolved matter should contain, so as to compare this quantity with that which was actually found.

The nitrogen of the skin of the specimen No. I. was 12·7680 p. c.

If we deduct the nitrogen of the persistent portion ..... $58{\cdot}88 \times \frac{18{\cdot}272}{100} = 7{\cdot}1845$

the soluble matter should have given 12 p. c. of nitrogen instead of 6·469, or for the total quantity dissolved $41{\cdot}12 \times \frac{12}{100} = 4{\cdot}9585$

The analysis only gave..... $18{\cdot}46 \times \frac{5{\cdot}112}{100} = 0{\cdot}9437$

and the total loss is in weight .... 22·66, & in nitrog. 4·0098 p. c.

In other words, the loss of weight was nearly half, and that of nitrogen more than four-fifths.

For No. III. the skin gave, of nitrogen..... 12·420 p. c.

and the persistent portion..... $48{\cdot}8 \times \frac{13{\cdot}59}{100} = 6{\cdot}663$

The soluble matter should have given for 51·2 dissolved = 5·757

or 11·244 per cent. Analysis gave.. $28{\cdot}75 \times \frac{7{\cdot}151}{100} = 2{\cdot}056$

The total loss of weight is therefore 22·45, & of nitrog. 3·701 p. c.

In other words, the loss of weight is nearly half, and that of nitrogen more than two-thirds.

Conclusions.

1. The skin of the Ox contains persistent portions which are

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strongly aggregated, and portions with a less degree of aggregation and with peculiar properties.

2. During its action on the skin, the tannin combines with both portions of the skin; saturation always occurs long before the period assigned to a good tanning; for each of the two parts it requires quantities of tannin considerably less than that of the gelatine.

3. The less aggregated parts of the hide form with the tannin a compound which is soluble in ammonia, which is altered by this solution, and undergoes a considerable loss of nitrogen during its evaporation to dryness.

4. Long-continued tanning causes the gradual solution of the less aggregated parts combined with the tannin, and in consequence the proportional increase of the quantity of the persistent fibrous matter. The product in this case must be more supple (or less brittle) and more tenacious.

5. The friable soluble portion which remains in tanned skins is unstable; in its dissolution it may carry with it considerable portions of the azotized substance.

Questions to be solved.

Cannot we succeed œconomically in removing a portion of the friable matter by means of slightly ammoniacal liquids, when the tannin has thoroughly saturated the skin, so as to avoid the prolongation of the tanning operation?

Would not the fragments of leather be adapted for manure, by adding to them an ammoniacal water, which would greatly hasten their decomposition?

The author thinks that from their more ready alterability, the less aggregated parts of the skin must be acted upon, combined, and partially dissolved by the contact of the agents employed in the different operations undergone by the skins. As regards tanning, properly so called, what are the effects produced by lime and soda, by the ammonia the formation of which is caused by these bases, and by dilute sulphuric and lactic acids?

As to the ordinary operations in the manufacture of wash-leather, the mechanical and chemical actions employed in presence of oil and weak solutions of potash,—is not their effect the solution of the disaggregable portion, so as to allow the persistent portion to predominate, the interposition of a saponaceous matter, which prevents the adherence of the fibres, and thus renders the skins more supple and spongy, at the same time leaving them of a sufficient degree of tenacity? As regards the operations of the tan-yard, the acidulated bath and the lactic fermentation must remove a portion of the less aggregated substance; the solution of the aluminous salt appears to have the effect of contracting and preserving the persistent parts, and what remains of the less aggregated parts; and lastly, the mixture of amylaceous, albuminous, and fatty substances would leave lubrificant matters between the fibres, which would allow them to glide one upon the other, so as to complete the means of softening and preserving skins of this kind.—*Comptes Rendus*, Nov. 17, 1856, p. 933.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On some new Facts regarding Iodide of Silver and the Metallic Fluorides. *By* H. SAINTE-CLAIRE DEVILLE.

IN the natural family of chlorine, bromine, iodine and cyanogen, it has been very positively and generally asserted that each of these bodies will expel those which follow it in the above series from their combinations. The author's object in the present paper is to show that there are some curious exceptions to this rule, as regards not only the chlorides and other halogenous bodies, but also the fluorides, the properties of which often by no means correspond with their probable composition. Thus there are special affinities, some of which are well known, such as the affinity of cyanogen for mercury, which, in presence of water, removes the potassium and sodium from the alkaline cyanides. The author has found that iodine and silver possess such an affinity for each other as to form an exception to the rule above alluded to.

Some time ago he showed that concentrated liquid hydriodic acid dissolves pure silver, with a violent evolution of hydrogen. By this reaction, transparent voluminous crystals of iodide of silver are obtained. Wishing to reproduce the native chloroiodide of silver, he exposed silver to the action of a mixture of muriatic and hydriodic acids, but only iodide of silver was obtained. He then treated dry precipitated chloride of silver with concentrated hydriodic acid. The chloride became heated nearly like lime in process of slaking, and iodide of silver was obtained. The muriatic acid was driven off in a few moments in the state of gas. Iodide of potassium, dissolved in water, is rendered alkaline by metallic silver; iodide of silver is formed. Iodide of potassium, fused in a porcelain crucible and kept at a cherry-red heat in contact with metallic silver, is decomposed in considerable quantity. After the experiment, a transparent globule of silicate of potash is found at the bottom of the crucible, and sometimes a black ring, which betrays the production of silicium at the expense of the substance of the crucible, and consequently that of potassium at the expense of the iodide. A considerable quantity of iodide of silver may also be observed in the mass of unaltered iodide of potassium.

Anhydrous chloride of aluminium combines with the alkaline chlorides, with evolution of heat; and the sesquichlorides of iron

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and chromium possess the same property, so that with sesquichloride of iron and chloride of sodium, a substance may be obtained which is fusible at about 392° F. and very fluid at this temperature. The corresponding compound of chrome is green, and soluble in water; whilst the sesquichloride from which it is prepared is violet and insoluble, so that the chrome has changed its molecular state in passing into the new combination. The peculiar affinities of these sesquichlorides in presence of the alkaline chlorides furnish an additional reason in support of the general classification proposed by M. Dumas*. Compounds of the same kind exist amongst the fluorides, of which cryolite is an example. When it is attempted to decompose cryolite at a high temperature by muriatic acid, this double fluoride of aluminium and sodium is not converted into a double chloride, but chloride of sodium is formed, and the fluoride of aluminium remains intact.

Fluor-spar is readily converted into chloride of calcium by gaseous muriatic acid at a high temperature, furnishing a source of anhydrous hydrofluoric acid, which was employed by the author in the following experiments.

A mixture of fluor-spar and alumina contained in a charcoal tray, introduced into a tube of the same substance, and treated with gaseous muriatic acid at the temperature of fusion of brass, furnishes chloride of calcium, and fluoride of aluminium is volatilized in large cubic crystals of great beauty. The same takes place in the production of sesquifluoride of chromium, but this only volatilizes at a much higher temperature. Thus muriatic acid decomposes the alkaline fluorides, and does not alter the sesquifluorides, which sublime in the midst of the acid gas brought to a very high temperature.

By treating a mixture of felspar and fluor-spar in the same way, the result obtained is, besides chloride of calcium, chloride of potassium arising from the felspar, and a very complex crystalline compound, which the author has not been able to analyse. It contains fluorides of silicium, aluminium and calcium, the latter no doubt derived from the excess of fluor-spar. When a mixture of clay and fluor-spar is treated in the same way, the volatile products are gaseous fluoride of silicium and fluoride of aluminium, which condenses.

The author obtained the anhydrous sesquifluorides of iron and chromium in the following manner; they were not previously known in the crystalline form. If calcined sesquioxide of iron be placed in a platinum crucible and moistened with hydrofluoric acid, the mixture becomes excessively heated, as is the case with alumina. When an excess of acid had been added and the material dried, the crucible is brought to a cherry-red heat. The fluoride then fuses and becomes partially volatilized, and the small cubical crystals of a

* The author has succeeded in preparing a fusible and crystallizable double sulphuret of aluminium and potassium, which violently decomposes water, by passing vapour of sulphur over a strongly-heated mixture of charcoal and sulphate of alumina and potash.

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transparent and nearly colourless fluoride of iron may be easily distinguished in the mass. The sesquifluoride of chromium is obtained in the same manner, except that hydrated oxide must be made use of. This fluoride is fusible and crystallizable, either by the cooling of the fused material, or by volatilization, which only takes place at the temperature of fusion of steel. The crystals are octahedra, and apparently regular; but they are too small to be measured, and possess too much colour to allow their influence upon polarized light to be studied. They are of a fine green colour, like oxide of chrome.

Such are the special affinities manifested in the exceptional properties of these fluorides. First, the fact of their production by hydrofluoric acid; the extraordinary evolution of heat which takes place on the contact of this acid with strongly-calcined oxides of aluminium and iron, which calcination has rendered completely indifferent at ordinary temperatures; then the resistance of the sesquifluorides to the action of gaseous muriatic acid at a high temperature; and lastly, the curious observation made by Berzelius, that alumina deprives the alkaline fluorides of a portion of their fluorine, rendering them caustic.—*Comptes Rendus*, Nov. 17, 1856.

Note on the Action of Iodide of Starch upon different Salts.
By F. Pisani.

Iodide of starch, poured into solutions of various salts, is decolorized in some cases, whilst in others it retains its blue colour. Silver-salts immediately decolorize iodide of starch, but the salts of lead and copper have no action upon it. Besides silver, this decolorization is produced by mercury, tin (protosalts), antimony (sesquichloride), arsenic (arsenious acid and chloride, $AsCl^3$), gold (perchloride), iron (protosalts), and manganese (protosalts).

Iodide of starch enables us to distinguish a protosalt of mercury from a persalt; with the former, decolorization takes place, at the same time that yellow iodide is precipitated; with the persalts there is no precipitate.

The protosalts of tin destroy the colour; the persalts do not. Arsenious acid and the corresponding chloride decolorize iodide of starch. With arsenic acid no effect is produced.

When the metals which decolorize iodide of starch are brought to their maximum of oxidation by nitric acid, only silver and mercury retain this property. The action of these metals is easily understood, when we consider their great affinity for iodine. Vauquelin observed that in triturating nitrate of mercury with iodine, iodide and perhaps iodate of mercury was formed. If a crystal of iodine be placed in a solution of pernitrate of mercury, red iodide is seen forming at the surface, whilst a lighter white powder is produced, which is the iodate. The same reaction takes place with iodine and nitrate of silver; the iodine soon becomes surrounded by a yellow halo, which gradually increases. M. Deville has lately shown the affinity of silver for iodine, as even the chloride of silver is decom-

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posed by the action of hydriodic acid. It is still more singular that iodide of starch, agitated with chloride of silver, yields its iodine and converts the metal into iodide. The filtered liquid contains chlorine, and the colour disappears.

Iodide of starch is the most sensitive reagent for detecting silver, providing mercury is not present. Thus it is sufficient to add $\frac{1}{5}$th of a cubic centimetre of iodide of starch to 100 cub. centims. of a liquid containing $\frac{1}{10}$ milligrm. of silver to cause immediate decolorization; the same quantity of iodide of starch gives a very perceptible colour to 100 cub. centims of pure water. In a liquid of less volume, $\frac{1}{100}$ milligrm. of silver may be detected.

The presence of silver in commercial lead may be immediately detected by dissolving it in nitric acid, leaving the liquid to cool, and adding a little iodide of starch. The only precaution necessary is to saturate the excess of acid with carbonate of lime, to avoid action upon the iodine.—*Comptes Rendus*, Dec. 15, 1856, p. 1118.

Note on the Colchicum autumnale. *By* L. Oberlin.

In 1820, after the chemical examination of several plants of the family *Colchicaceæ*, MM. Pelletier and Caventou* assimilated the principle found in the *Colchicum autumnale* to that discovered by them in other plants of this family, and indicated the presence of veratrine in this plant.

In 1833, MM. Hess and Geiger† pointed out the difference which separates the active principle of the *Colchicum* from that contained in White Hellebore and Sabadilla, and described the physical and chemical characters of the alkali, which they called colchicine. I have resumed this investigation; but although I have carefully followed the process of extraction which they state they employed, I have not obtained a crystallizable principle, even by trying all the solvents to facilitate crystallization, and two chemists who have repeated the experiment at my request have arrived at the same result as myself. The following are the results of my researches upon this uncrystallizable product, obtained by the process of MM. Hess and Geiger.

The aqueous solution of colchicine, acidified by sulphuric or muriatic acid, acquires an intense yellow colour when it is brought to a certain state of concentration on the sand-bath; it gives a yellowish-white precipitate with water; this precipitate, when well washed and freed from the colouring matter, is soluble in alcohol or æther, and crystallizes readily. A larger quantity of the product is obtained by employing muriatic acid, and allowing the reaction to take place spontaneously. After a few weeks, a great many warts with an acicular crystallization are found. These, when pulverized and well washed, furnish a nearly white product after the first recrystallization; whereas, when sulphuric acid is employed, white nacreous crystals cannot be obtained without great trouble, the resinous

* Ann. de Phys. et de Chim., xiv.

† Handwörterbuch der reinen und angewandten Chemie, ii. p. 330.

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colouring matter which accompanies this product being got rid of with difficulty.

This crystalline principle is not a salt; it is neutral, and reagents do not indicate any trace of the acids employed in its preparation. I call it *colchiceine*, as it differs from the colchicine of Hess and Geiger, which, as I shall show, appears to be a complex product.

The properties of colchiceine are as follows:—It crystallizes very readily in nacreous lamellæ; it is almost insoluble in water, but communicates to this vehicle a slight bitterness, which is perceptibly increased by ebullition. At this temperature a considerable portion of the product is dissolved, but this is deposited immediately after refrigeration. The solvents of colchiceine are alcohol, æther, methylic alcohol and chloroform, which when in contact with it acquire a very intense and persistent bitterness.

The alcoholic solution of colchiceine is coloured by the addition of bichloride of platinum, and no precipitate is formed. Pure and concentrated nitric acid dissolves colchiceine; it acquires a very intense yellow colour, passes to violet, then to deep red and bright red, and returns to its original yellow colour.

Concentrated sulphuric acid dissolves it, forming a solution of a very intense yellow colour, which is retained even after dilution with water; in course of time brownish flakes are formed. Muriatic acid dissolves it with a bright yellow colour. Lastly, acetic acid also dissolves it, but without alteration of colour.

Colchiceine is soluble in ammonia, and crystallizes by evaporation in the air; it is soluble in caustic potash, acquires a green colour with perchloride of iron, and presents no change of colour or turbidity in presence of solutions of neutral or tribasic acetate of lead, of nitrate of silver, of perchloride of mercury, or infusion of nut-galls.

Colchiceine appears to be capable of combining with baryta; if saturated solutions of hydrate of baryta and colchiceine in methylic alcohol be mixed together, a voluminous precipitate is soon formed; this is gelatinous and soluble in wood-spirit, and even in an excess of the solution of baryta.

Colchiceine is unalterable in the air, and has no action upon red or blue litmus-paper. When exposed in a tube to the heat of the oil-bath, it softens at first, and fuses at 311° F.; if the temperature be raised, it becomes coloured at about 392° F. When heated upon a platinum plate, it fuses, acquires a yellowish colour, and burns, leaving only a trace of a spot which has no action upon moistened test-papers. When heated with caustic potash, it evolves a gas which renders reddened litmus-paper blue. When calcined with potassium, according to the process of M. Lassaigne, a residue is obtained, which, treated with a solution of a sesquisalt of iron and afterwards with muriatic acid, furnishes a blue liquid, the deposit from which is prussian blue.

The presence of nitrogen being proved by these two experiments, I submitted colchiceine to elementary analysis, with the following results:—

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	Calculation.	Experiment (average).
C	62·83	62·669
H	6·60	6·560
N	4·19	4·298
O	26·38	26·473

Pre-existence of Colchiceine in the Seeds of Colchicum.—As this substance might be the result of the action of reagents upon the normal materials of the seeds of the *Colchicum*, I endeavoured to ascertain its pre-existence, and believe I have succeeded by proceeding in the following manner.

I dissolved the alcoholic extract of the seeds of *Colchicum*, previously freed from oil and starchy matter, in alcohol, and decolorized it by well-washed charcoal; after filtration, the charcoal was treated repeatedly with boiling alcohol, which was added to the first liquid. The syrupous extract which remained after distillation, when dissolved in water and slightly acidulated with very dilute sulphuric acid, gives rise to a flocculent precipitate; the liquid, when filtered and left for some weeks, produces the warty crystals previously described. These crystallize in alcohol, and are identical with colchiceine.

The action of acids upon analogous bodies having given rise to decompositions producing peculiar principles and glycose, I endeavoured to ascertain the presence of the latter in the mother-liquors from which the crystals of colchiceine were deposited, but I only succeeded in isolating a resinous matter, insoluble in water, combined with some colouring matter and very soluble in alkalies, a product consequently of an acid nature. The characters of this resinous matter are, that it is soluble in alcohol and æther, acquires a blood-red colour with nitric acid, and dissolves in ammonia, to which it also gives an intense red colour.

Physiological Experiments.—According to experiments made by Prof. Schroff* of Vienna, the colchicine obtained according to the process of Hess and Geiger has a poisonous action upon rabbits even in doses of 0·01 grm.; the animal only dies in from twelve to eighteen hours. Given in large doses, even of 1 grm., it does not produce death in less than seven or eight hours. When colchiceine is injected into the stomach in a dose of 0·01 grm., the animal does not die for ten or twelve hours, but in a dose of 5 centigrms. it causes a complete paralysis of the members and death in a few minutes.—*Comptes Rendus*, Dec. 29, 1856, p. 1199.

On the Rational Constitution of Fulminic Acid, and a new Series of Bodies derived from Acetic Acid. By L. Chichnoff.

According to my recent researches, I have just arranged three bodies already known, in the numerous series of bodies derived from cyanic acid, or rather from ammonia; these are *trigenic, fulminic* and *isocyanuric acids.*

* Oesterreich. Zeitschr. für prakt. Heilkunde, June 6, 1856.

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In my previous memoir on the fulminates, I have already put forward the opinion, that fulminic acid splits into isocyanuric and cyanic acids when we endeavour to replace all its hydrogen by an alkaline metal. Liebig having taken a different view of this reaction in his memoir, I have been obliged again to have recourse to experiments, to try to support this fact with new proofs. I have thus succeeded in ascertaining the presence of cyanic acid by the ordinary reagents in the products of the decomposition of fulminic acid under the action of the alkaline chlorides and iodides upon the fulminates.

As to the second equivalent of cyanic acid, I have been able to prove its presence in isocyanuric acid by the ready formation of cyanates of potash and urea on heating the isocyanurates of potash or ammonia. Moreover, the reaction of Gladstone, in which urea and sulphocyanic acid are produced when a fulminate of ammonia and copper is treated by sulphuretted hydrogen, and the decomposition of fulminate of mercury by caustic potash with formation of cyanate of potash, fully verify this pre-existence of the cyanic acid groups in the fulminates; at the same time, the separation of fulminic acid into isocyanuric and cyanic acids, is a proof that fulminic acid really contains 2 equivs. of cyanic acid, as is required by the formula

$$(CyO^2H)^2, NC^4H^2(NO^4).$$

As to the latter supposition, that is to say, the pre-existence of the group mononitro-acetonitryle in fulminic acid, I have succeeded in proving it by the action of a mixture of sulphuric and nitric acids upon isocyanuric acid.

In this case, in fact, I obtained, on the one hand, the products of the decomposition of cyanic acid, namely carbonic acid and ammonia, and on the other, in place of the body mononitro-acetonitryle, a substance which was shown by its analysis and reactions to be trinitro-acetonitryle, $NC^4(NO^4)^3$:—

$$CyO^2H, NC^4H^2(NO^4) + 2NO^6H = C^2O^4 + NH^3 + H^2O^3 + NC^4(NO^4)^3.$$

Isocyanuric acid, treated with hypochlorite of lime, furnishes directly chloropicrine, $C^2(NO^4)Cl^3$, that is to say, a nitrated body. The isocyanurates absorb nascent hydrogen, with reduction of the group NO^4, for the new products formed no longer possess the original property of exploding by heat.

Besides this, the analysis of the isocyanurates by means of soda-lime does not furnish more than two-thirds of the nitrogen in the form of ammonia. From all this, the formula of fulminic acid would be

$$(CyO^2H)^2NC^4H^2(NO^4),$$

derived from three molecules of ammonia, or more directly from the biuret—

$$(CyO^2H)^2NH^3.$$

It is easily seen that the isomerism of fulminic and cyanic acids is purely accidental, for if, instead of containing a single group NO^4, fulminic acid contained two or even three, the isomerism would no longer exist.

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Trigenic acid is formed by the action of cyanic acid upon aldehyde, with evolution of carbonic acid:—

$$\underset{\text{Aldehyde.}}{\left.\begin{matrix} C^4\,H^3 \\ H \end{matrix}\right\}}\,O^2+\left\{\begin{matrix} C^2\,O^2\,NH \\ C^2\,O^2\,NH \\ C^2\,O^2\,NH \end{matrix}\right\}=C^2\,O^4+\underset{\text{Trigenic acid.}}{\left\{\begin{matrix} C^4\,H^3\,NH^2 \\ C^2\,O^2\,NH \\ C^2\,O^2\,NH \end{matrix}\right\}}$$

According to the composition attributed to fulminic acid, I think its formation may be explained in an analogous way to that of trigenic acid. Thus—

$$\underset{\text{Nitro-acetic acid.}}{\left.\begin{matrix} C^4\,H^2\,(NO^4) \\ H \end{matrix}\right\}}\,O^4+\left\{\begin{matrix} C^2\,O^2\,NH \\ C^2\,O^2\,NH \\ C^2\,O^2\,NH \end{matrix}\right\}=C^2\,O^4+H^2\,O^2+\underset{\text{Fulminic acid.}}{(CyO^2\,H)^2NC^4\,H^2\,(NO^4)}.$$

Thus, on the one hand, there would be formation of nitro-acetic, on the other of cyanic acid, and mutual reaction between these bodies. The residue of the cyanic acid being discoverable in the fulminic acid, renders this supposition very probable.

Besides, the formation of hydrocyanic acid in the products of the oxidation of alcohol by nitric acid is well ascertained, and cyanic acid is only an acid of the former. This formation of cyanic acid may be represented by the following equation:—

$$C^4\,H^6\,O^2+2NO^3=2CyO^2\,H+2H^2\,O^2,$$

an equation which, as is well known, is not new in chemistry.

Trinitroacetonitryle is solid at the ordinary temperature, fusible at 106°·9 F., and decomposes at a temperature of 428° F. with a loud detonation and production of a blue flame. Water and alcohol decompose this body; anhydrous æther is its only solvent without decomposition.—*Comptes Rendus*, Jan. 5, 1857, p. 14.

On the Action of some Reagents upon Aluminium in the dry way. *By* C. *and* A. Tissier.

Aluminium is capable of becoming oxidized at a high temperature, such as that of welding iron, but the oxidation is limited by the thin stratum of alumina which forms on the surface of the metal.

Aluminium decomposes the oxides of copper and lead with explosion; it only partially decomposes oxide of iron in such a manner that it may form an alloy of equal equivalents with that metal; it has no action on the oxides of zinc and manganese.

Aluminium heated in fused nitrate of potash burns with deflagration, accompanied by a fine blue light. This is also the case with sulphate of potash or soda, with which it produces a strong detonation.

The action of carbonate of potash, although less energetic than that of the preceding, is still sufficiently so to oxidize the metal rapidly, with deposition of carbon. The alkaline silicates and borates, including glass and borax, attack the metal, with deposition of boron and silicium. The latter, although it surrounds the metal as it is

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oxidized, does not appear to combine with it under these circumstances, for the metal which remains has lost none of its malleability.

Chloride of sodium and fluoride of calcium (especially the latter) constitute the best fluxes for the new metal.—*Comptes Rendus*, Dec. 29, 1856, p. 1187.

On the Preparation of pure Grape-Sugar. *By* EMIL SIEGLE.

Commercial honey, as crystalline as possible, is spread upon porous tiles. The white crystalline residue is dissolved in alcohol, and purified by recrystallization; if necessary, also with animal charcoal. The honey yields about one-fourth of its weight of grape-sugar.—*Journ. für Prakt. Chem.*, lxviii. p. 148.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Experiments on the Purification of Oxide of Uranium, and Preparation of Subsidiary Products from the Uranium Ores of Joachimsthal. *By* M. PATERA.

IN an official report the author has described the processes for obtaining oxide of uranium free from arsenic, and at the same time procuring vanadium as a subsidiary product.

The impure samples of uranium-yellow contain, according to the analyses of E. Wysoky, 6·69, 6·52, 5·60 of arsenic acid. From the high price of uranium-yellow, it would not be advisable to bring such impure products into the market; the problem was therefore to remove the arsenic in a simple and certain manner from the oxides, and at the same time to furnish a means by which in future the presence of such a considerable amount of arsenic might be avoided.

Arsenic acid forms a pale yellow salt with oxide of uranium; this is difficult to decompose, dissolves in acids and also in an excess of carbonate of soda, and therefore behaves nearly like pure uranium-yellow, except that the arseniate of uranium is rather less soluble in both solvents.

There would be great difficulty in removing the arsenic acid as sulphuret of arsenic by sulphuretted hydrogen gas, because it is difficult to decompose in this way; the yellow peroxide of uranium would also be converted into green protoxide, which must be again oxidized.

Patera therefore first of all attempted to combine the arsenic acid with peroxide of iron, by dissolving the impure uranium-yellow in sulphuric acid, adding a solution of perchloride of iron to the acid solution, then precipitating the uranium with solution of carbonate of soda, and dissolving it again in an excess of the latter. The solution was boiled, when the arseniate of iron separated completely with the excess of peroxide of iron added.

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On the small scale there was no objection to this process, but on the large scale the quantity of the ferruginous precipitate was troublesome. Although the uranium-yellow obtained in the ordinary way from the solution was very pure and had a beautiful colour, this method, which in many cases may be very serviceable, was abandoned and another way adopted, in which corresponding results were soon obtained. The uranium-yellow was dissolved in sulphuric acid, but care was taken only to add so much of this that the entire mass was not dissolved. The arseniate of uranium, as already stated, not being so readily soluble as the uranium-yellow, the greater part of that salt remained undissolved. For the same reason, by careful supersaturation with carbonate of soda, the greater part of the arseniate of uranium dissolved in the sulphuric acid could be separated again, whilst the pure oxide of uranium readily dissolved in the soda. These two products, in which nearly all the arsenic in the uranium-yellow to be purified was concentrated, were mixed and operated upon together.

The quantitative analysis made of them by E. Wysoky gave 59·35 of oxide of uranium, 27·98 of arsenic acid, and 12·50 of water; this composition corresponds pretty well with the formula $(Ur^2O^3)^2$, AsO^5+6Aq.

To get rid of the arsenic acid from this product by a process easily effected technically, it was finely powdered, calcined for several hours, first with charcoal-dust, and afterwards with 15 per cent. of dehydrated carbonate of soda, with which a little nitrate of potash was mixed, and after calcining lixiviated with hot water. The water dissolved the arseniate of soda, and with it also soda-salts of rare metallic acids, especially vanadiate of soda. The uranium-yellow obtained from the residue was perfectly free from arsenic. An experiment was then made also with a hundredweight of rich uranium ore, which was calcined with carbonate of soda instead of with lime, then lixiviated with hot water and dissolved in acid. The arsenic of the ore could thus be completely got rid of, and the ore dissolved in acid could be very quickly worked, as no sulphate of lime was present to hinder the washing. The residue of the ore only contained imponderable traces of uranium. The employment of carbonate of soda instead of lime in the calcining would certainly cause a slight increase of expense; but this need hardly be taken into consideration, as labour is saved by the easier washing; a pure product free from arsenic is obtained, and vanadic acid, which is still so rare, is procured without any further considerable expense. The solution obtained by the washing with water has only to be evaporated to dryness; and certainly every scientific establishment would purchase this saline mass at the cost of the slight extra expense, if we do not specially take into consideration the vanadic acid, which, although not yet employed in the arts, bears a high price on account of its rarity.

In conclusion, attention is drawn to the utility of this method of separating the last portions of arsenic from an arsenical compound (*Speise*); it will be of especial use to the manufacturers of nickel.

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It is certainly easy, by calcining with charcoal, to volatilize the greater part of the arsenic; but a considerable portion of it remains obstinately with the nickel, and is difficult of separation therefrom even in the humid way. This contamination, which is exceedingly injurious to the goodness and applicability of nickel, is completely got rid of by the process above described, which presents no technical difficulties, and is both accurate and inexpensive.

To obtain the vanadium, the uranium ore is first calcined dead, in order to get rid of the sulphur, arsenic, and molybdenum contained in it as completely as possible; it is then calcined for an hour with 15 per cent. of carbonate of soda and 2 per cent. of nitrate of potash. In this way acid uranate of soda is formed, and then arseniate, vanadiate, molybdate, and some silicate of soda. If the calcined mass be now lixiviated with hot water, the uranate remains undissolved; whilst the soda-salts of arsenic, vanadic, molybdic and silicic acids, as well as the undecomposed carbonate of soda, are dissolved. The residue containing the uranium is used for the preparation of uranium-yellow, and the liquid is operated upon for vanadium. It would not be advisable to hand over this liquid to the chemical laboratories for the preparation of vanadium, because the amount of vanadium in the ore is very small, hardly exceeding that of the iron-ores containing vanadium of Sweden and the Harz, which Bodenmann describes as containing 0·2 per cent. of vanadic acid. If we suppose this amount to be completely extricable from the ores of Joachimsthal, we should get by evaporation from 1 cwt. of uranium ore a saline mass of about 20 lbs, which would contain about 3 oz. (6·4 loth), that is to say 1 per cent. of vanadic acid. Few laboratories are adapted for operating upon such large masses of salts; it therefore appeared desirable to concentrate the vanadium quickly, and without loss or great expense, into a smaller saline mass.

With this view, Patera made a series of experiments with the methods employed in analytical chemistry in the determination of vanadium, in order to employ one or other of them on a large scale. By the precipitation of vanadic acid with muriate of ammonia, a pure product is certainly obtained, but a large quantity of the acid remains in solution, and this can hardly be procured, as the quantity of salt is increased by the muriate of ammonia. Vanadium might also be obtained in the form of sulphuret, by supersaturating the solution of the vanadiate with an alkaline sulphuret, when sulphuret of vanadium is dissolved, and can be again thrown down as brown sulphuret of vanadium by supersaturating the solution with a dilute acid. In this case also a great deal of vanadium remains in solution in the form of vanadious acid, by which the solution appears of a more or less blue colour; but this operation would also be very inconvenient on a large scale and even dangerous, on account of the great evolution of sulphuretted hydrogen gas.

Pyrites are often intermixed with the ores of uranium; in roasting, sulphates are then formed, and these pass over into the lye. A precipitation of the vanadic acid by a baryta-salt would therefore be very dear and furnish a very impure product; moreover, this pre-

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cipitation is far from being complete. Precipitations with mercurial salts also are not applicable on a large scale.

Patera therefore made use of the well-known reaction of tincture of galls, which furnishes a deep blue solution with vanadiates, but only succeeds when the solution is perfectly neutral. It is, however, inapplicable to the preparation of vanadium, because no precipitate is produced. But if a solution containing vanadium be acidified with an acid, such as muriatic acid, then mixed with decoction of galls and carefully neutralized with soda, a dark blue voluminous precipitate of tannate of vanadium is thrown down, which settles quickly and may be easily filtered.

With it, tannate of soda, and some compounds of molybdenum, arsenic, uranium, and silica are also thrown down. The deep indigo-blue precipitate contracts greatly in drying and becomes black; if it be calcined, the tannic acids are burnt away, some arsenic and molybdenum are evolved, and there remains an impure vanadiate of soda, with which vanadite is probably mixed; this crude product may then be employed in the preparation of pure vanadium compounds.

From a hundredweight of uranium ore 9 oz. (18 loth) of the tannate were obtained on an average; after calcination, these gave 5 oz. (10 loth) of the above crude product.

The expenses of its preparation are not much higher than the simple evaporation of the lye; the expense of the first calcining with carbonate of soda and nitrate of potash and the washing with hot water are connected with the manufacture of uranium-yellow; the labour specially relating to the vanadium is therefore very small, and may easily be performed by the same workmen who are engaged in the manipulation of the uranium. In the preparation of the tannic acid compound from the saline solution from 1 cwt. of ore, there are employed—

2 lbs. of muriatic acid at 5 kr.	10 kr.	(4*d.*)
1 lb. of gall-nuts at 30 kr.....	30 kr.	(12*d.*)
4 lbs. of carbonate of soda at 6 kr.	24 kr.	(9½*d.*)
Total.....	1 fl. 4 kr.	(2*s.* 1½*d.*)

The new apparatus necessary is limited to a few wooden tubs and linen filtering bags.

The advantages of the method described are simplicity and cheapness, combined with great exactness. The crude product obtained at a cost of about 2*s.* 1½*d.* contains about 30 per cent., or rather more vanadic acid; the pound of vanadic acid in the crude product cannot therefore cost much more than one pound; and the work at the same time is so simple, that it can be performed with ease by any skilful operative, and the vanadium contained in the liquid is so completely collected in the crude product, that not a trace can be detected in the fluid filtered from the blue precipitate when the point of neutralization has been correctly found. The reaction is so delicate, that the small quantities of vanadium which remain with uranium in the solution of sulphate of soda left as a mother-liquor in the manu-

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facture of uranium-yellow, may be obtained from it. The loss by waste is very small, as the precipitate of tannate of vanadium is exceedingly voluminous in the moist state, and contains comparatively very little vanadium. According to an approximative valuation (the quantitative determinations of vanadium being all very imperfect), the uranium ore of Joachimsthal contains 0·2 per cent. of vanadic acid; and as 30 to 50 cwts. of this ore are worked annually, the quantity of vanadic acid obtained would amount to about 10 lbs. in the year, which is certainly a large quantity considering the rarity of the substance.—*Oesterreich. Zeitschrift für Berg- und Hüttenwesen*, 1856, No. 31.

On a Method of imparting a Red Colour to Bone and Ivory. *By* Dr. J. C. Kellermann.

The bone to be coloured is laid for fifteen to twenty minutes in very dilute cold nitric acid of the strength of a good vinegar; this dilute nitric acid is obtained by mixing fully ½ a litre of soft water with about 13 grms. of nitric acid. The bone is then immersed for fifteen to twenty minutes in a solution of protochloride of tin, made by dissolving a piece of the size of a lentil in a pint of water. The objects thus mordanted are then put into the following red-bath, which must first be heated until it begins to boil.

Red-bath.—For an experiment on the small scale, take 3 to 5 grs. of fine red carmine, pour to it 10 to 12 drops of ammonia, and stir it up well until the carmine is dissolved; then add about 2 oz. of soft water. In this bath, when heated to boiling, the objects must be left for about fifteen minutes. The tints obtained are more vivid when the boiling of the bath is not continued whilst the objects are in it.

If it be desired to change the tint thus obtained (a very fiery carmine-red) to a more scarlet colour, one of the following methods may be employed. When the red-bath begins to boil, and immediately after the objects have been immersed in it, 5 to 10 drops of tartaric acid of the strength of a good vinegar may be added; or the water in which the protochloride of tin is to be dissolved may be mixed with an extremely small quantity of English sulphuric acid.—Dingler's *Polytechn. Journal*, cxli. p. 67.

PROCEEDINGS OF SOCIETIES.

Royal Society.

December 11, 1856. (General Sabine, R.A., V.P. and Treasurer, in the Chair.)

"On the Existence of Silver in Sea-water." By Frederick Field, F.C.S.

In a paper published by MM. Malaguti, Durocher, and Sarzeaud in the 'Annales de Chimie et de Physique,' xxviii. p. 129,

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there is an account of the detection and estimation of silver in sea-water. The authors suspected the existence of the metal from the extensive diffusion of silver in the mineral kingdom, the conversion of its sulphide into chloride by the prolonged action of soluble bodies containing chlorine, and the solubility of chloride of silver in chloride of sodium. The method pursued was by passing sulphuretted hydrogen through large quantities of water, and also by fusing the salts obtained by evaporation with litharge and subsequent cupellation.

As a solution of chloride of silver in chloride of sodium is instantly decomposed by metallic copper, chloride of copper being formed and silver precipitated, it appeared to me highly probable that the copper and the yellow metal used in sheathing the hulls of vessels, must, after long exposure to sea-water, contain more silver than they did before having been exposed to its action, by decomposing chloride of silver in their passage through the sea, and depositing the metal on their surfaces. A large vessel, the 'Ana Guimaraens,' now under the Chilian flag, was hauled down in the Bay of Herradura, near Coquimbo, for the purpose of being repaired, and the captain obligingly furnished me with a few ounces of the yellow metal from the bottom of the vessel. The investigation was interesting, as the metal had been on for more than seven years (an unusually long period), and the ship had been trading up and down the Pacific Ocean all that time. The metal, upon examination, was found to be exceedingly brittle, and could be broken between the fingers with great ease. 5000 grs. were dissolved in pure nitric acid and the solution diluted; a few drops of hydrochloric acid were added, and the precipitate allowed to subside for three days. A large quantity of white insoluble matter had collected by that time at the bottom of the beaker. This was filtered off, dried, and fused with 100 grs. pure litharge and suitable proportions of bitartrate of potash and carbonate of soda, the ashes of the filter also being added. The resulting button of lead was subsequently cupelled, and yielded 2·01 grs. silver, or 1 lb. 1 oz. 2 dwts. 15 grs. troy per ton. This very large quantity could hardly be supposed to have existed in the original metal, as the value of the silver would be well worth the extraction. It is to be regretted that the captain had none of the original on board. A piece of yellow metal with which he was repairing the vessel yielded only 0 oz. 18 dwts. to the ton. I was enabled by the courtesy of the captain of the 'Nina,' a brig which had just arrived in the Pacific from England, to obtain more satisfactory information. He gave me a piece of Muntz's yellow metal from his cabin, from the same lot with which the brig was sheathed, but which had never been in contact with salt water; and also a small portion from the hull of the ship after it had been on nearly three years. The experiments were performed as before, and the results were very striking.

grs.		gr.		oz.	dwts.	grs.	
1700 from cabin	gave	·051	= ·003 per cent. =	0	19	14	per ton.
1700 from hull	„	·400	= ·023 „ =	7	13	1	„ „

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That which had been exposed to the sea having nearly eight times as much silver as the original sample.

Many other specimens were examined of metals from the bottoms of ships, and of pieces which are always kept on board in case of need, and it was invariably found that the former contained more silver than the latter. For instance, a piece from the hull of the 'Bergmann' gave 5 ozs. 16 dwts. 18 grs. per ton, while that from the cabin yielded 4 ozs. 6 dwts. 12 grs. 200 grs. from a piece from the hull of the 'Parga' gave ·072 gr., and a piece of fresh metal ·050; while from the 'Grasmere,' only coppered a few months, 610 grs. from the hull gave ·075 and from the cabin ·072,—a very slight difference indeed.

It will be observed that the amount of silver in the above specimens of fresh metal is very high, and it is probable that most of these are merely the re-rolling of masses of metal melted down from old sheathing, and have derived the greater part of their silver from the sea on former occasions. It is well known that the copper used in the manufacture of yellow metal is very pure, containing 2 or 3 dwts. of silver per ton, frequently not so much, and silver is very seldom associated with the other constituent, zinc. In order to arrive at more certain results, however, I have granulated some very pure copper, reserving some in a glass stoppered bottle, and suspended the remainder (about 10 ounces) in a wooden box perforated on all sides, a few feet under the surface of the Pacific Ocean. When occasion offers, the box is towed by a line at the stern of a vessel which is trading up and down the coast of Chili. It is almost too soon to expect any decisive results at present, but in a few months I hope to be enabled to send both the original copper, and that which has been exposed to the action of the sea.

January 22, 1857. (Dr. W. A. Miller, V.P., in the Chair.)

"On some of the Products of the Destructive Distillation of Boghead Coal."—Part I. By C. Greville Williams, Esq.

The paper, of which the following is a brief abstract, constitutes the first part of the author's examination of the hydrocarbons contained in boghead naphtha. In it he gives the results of his experiments on that portion of the fluid which resists the action of monohydrated nitric and sulphuric acids. He had previously stated the fact of his having obtained a substance possessing the composition and vapour-density of butyle*, and had expressed a belief that he should succeed in isolating not only that radical, but also propyle, amyle, and caproyle. The composition of the radicals varies so little, that to determine the boiling-points it was necessary to take the density of the vapour of all those fractions which distilled anywhere near their known boiling-points; and in each case he regarded that fraction which gave the nearest result as representing the boiling-point of the radical as obtained from the source mentioned.

* Chem. Gaz., vol. xiv. p. 19.

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Propyle presented itself under the form of a colourless, very mobile fluid, having a pleasant odour, and boiling at 68° C. At 18° it had the very low density of 0·6745. Combustion gave results agreeing closely with the formula

$$C^{12}H^{14}=4 \text{ vols.},$$

confirmed by a determination of the density of its vapour by Gay-Lussac's method, which gave 2·96, theory requiring 2·97. Propyle had not been previously obtained.

Butyle from the Torbane-hill mineral distils at 119°, and has a density of 0·6945 at 18°; its analysis coincided with the formula

$$C^{16}H^{18}.$$

The vapour-density was found to be 3·88, theory requiring 3·94.

Amyle distilled at 159°, and had a density of 0·7365 at 18°. On analysis, numbers were obtained agreeing perfectly with the formula

$$C^{30}H^{22}.$$

The vapour-density was found to be 4·93; theory requires 4·91.

Caproyle boiled at 202°; its density at 18° was 0·7568. The results of analysis accorded with the expression

$$C^{24}H^{26},$$

which indicates a vapour-density of 5·87, while experiment yielded 5·83.

The experiments detailed in the paper appear to demonstrate the radical nature of the hydrocarbons, and to negative the assumption of their being homologues of marsh-gas.

The paper concludes with a description of a method, by which, where numerous vapour-density determinations are to be made, the necessity is avoided of refilling the balloon with water or mercury in order to determine the residual air.

"On the Optical Characters of certain Alkaloids associated with Quinine, and of the Sulphates of their Iodo-compounds." By William Bird Herapath, M.D., in a Letter to Professor Stokes, Sec. R.S.

You will probably recollect that I sent you some time since a small portion of an alkaloid, which at that time was called quinidine in Germany, but it has since been distinguished from it and named cinchonidine. You then examined it for epipolism or fluorescence, and you pronounced the opinion that it possessed this property only in a minor degree, and you imagined that this arose from the presence of a small per-centage of α-quinine.

I have since obtained, through the kindness of Mr. J. E. Howard, specimens of the perfectly pure alkaloids quinidine and cinchonidine, and find that quinidine, which I can now identify as the β-quinine of Von Heijningen, possesses the phænomenon of fluorescence or epipolic dispersion as powerfully as α-quinine; whilst cinchonidine, if perfectly pure, is devoid of it altogether; and recent experiments have shown me that a small per-centage of quinidine was the cause of the epipolic dispersion found by you in the specimen of cinchonidine sent by me.

It may be as well to state that the cinchonidine tested by water of chlorine and ammonia gave no evidence of green tint, which it

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would have done if only $\frac{1}{5000}$dth part of either α-quinine or quinidine had been present, according to some recent experiments of my own.

I have also found that 1 gr. of pure quinine or quinidine in 35,000 of water will give an evident "*epipolic*" appearance; whilst when diluted with 70,000 grs. of water we have still very evident appearances of "fluorescence" upon the perpendicular wall of the glass vessel exposed to the incident light; whilst a bluish milkiness of "internal dispersion" may be seen when 1 gr. of either alkaloid is diluted with 700,000 grs. or 10 gallons of distilled water, well acidulated in all these cases with sulphuric acid.

Some other interesting results have followed from these investigations. When quinidine is dissolved in an excess of diluted sulphuric acid, and the solution mixed with about twice its bulk of spirit, and warmed to 130° F., and tincture of iodine then added in sufficient quantity, and subsequently set in repose, beautiful red acicular crystals are deposited; these, upon recrystallization from rectified spirit, acquire an increased size, become beautiful quadrilateral prisms, leaving a deep garnet-red by transmitted light, and possessing a clear bluish-purple reflected tint; they are optically doubly absorbent in a slight degree, and transmit a brownish-orange body-colour when polarized perpendicular to axis. The primary form appears to be a rhombic prism, and as far as my present analyses go, appears to possess centesimally the following composition:—

Iodine	39·665
Sulphuric acid	6·273
Carbon	32·890
Hydrogen	3·960
Nitrogen	4·400
Oxygen	5·040
Water	8·504
	100·712

The excess arises from the hydrogen twice calculated in water of crystallization.

These numbers agree very closely with the formula

$$(C^{35}\,H^{19}\,N^{2}\,O^{4} + I^{2})\,SO^{3}\,HO + 5HO,$$

and prove it to be the sulphate of iodo-quinidine, very analogous to the optical quinine compound, yet differing materially in its optical properties.

There is another alkaloid frequently associated with quinidine, which also crystallizes from spirit in the prismatic form like quinidine and cinchonidine, but is another example of epipolism or fluorescence. Its iodo-sulphate is deep olive-green in its reflected tint, orange-yellow by transmitted light, and possessing in an eminent degree optically doubly absorbent powers, thin laminæ being quite black, but still thinner ones give a bistre-brown "body-colour" when polarized perpendicular to axis.

This alkaloid was also furnished me by the kindness of Mr. Howard, but has not yet been sufficiently purified, or in the quantity necessary to give certain results.

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It possesses one very peculiar property. When dissolved in chloroform and evaporated spontaneously on glass, the gummy and uncrystalline residue, mounted in Canada balsam, at once shows a deep blue-green, epipolic, or fluorescent appearance.

Pure cinchonidine does not possess epipolic dispersion and does not become green by chlorine-water and ammonia; and when it is dissolved in acetic acid or chloroform and the fluid is exposed on glass plates to spontaneous evaporation, beautiful crystals in circular spots or drusæ develope themselves, which under polarized light exhibit black crosses and white or coloured sectors.

These appearances are not exhibited by pure quinine or true quinidine (β-quinine), both of which give a gummy, uncrystalline, and perfectly transparent residue.

Pure cinchonidine, thus optically and chemically distinguishable from either quinine or quinidine, is still further remarkable for producing with sulphuric acid and iodine an optical doubly absorbent compound of intense power, even equal to the sulphate of iodo-quinine compound; these crystals are very similar in form to my artificial tourmalines, and have long been mistaken by me for them; even at present I can only distinguish them by the tints in reflected light and the complementary body-colour, viz. whilst sulphate of iodo-quinine gives a cantharidine-green reflected tint, and a pink, ruby-red, reddish-brown or black body-colour when polarized perpendicular to the axis, according to the thickness of the plate examined, the sulphate of iodo-cinchonidine is golden-green by reflected light, and gives a sky or indigo-blue or black "body-colour" when polarized perpendicular to the axis. I have not yet made sufficient chemical analyses of this substance to enable me to decide on its formula, but I have obtained 39·307 per cent. iodine and 8·864 per cent. sulphuric acid, which sufficiently indicate a chemical difference in constitution from the sulphate of iodo-quinine, which, it may be remembered, contains 32·609 per cent. iodine and 10·61 per cent. sulphuric acid.

I hope soon to present these results in more detail when sufficient leisure is afforded me for the purpose.—W. B. H.

Meeting of German Naturalists.

[We are indebted to the kindness of Count Marschall for the following Notices of Chemical Communications made to the late Meeting of German Naturalists at Vienna.—Ed.]

September 16, 1856.

Prof. Wertheim of Pesth described a crystalline basic substance extracted from the hemlock (*Conium maculatum*) together with coniine, from which it was separated with great difficulty. The new base (*conhydrine*) is represented in its anhydrous state by the formula $C^{16} H^{17} NO^2$. It is obtained from the juice of the plant, previously supersaturated with hydrochloric acid, by the action of chloride of platinum. By separating the water, coniine may be obtained in the

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liquid state. The crystals of conhydrine and of hydrochlorate of conhydrine both belong to the binary (prismatic) system.

September 17.

Prof. Wittstein gave notice of a new sort of Peruvian bark (*China pseudo-regia*), and of an alkaloid, *cinchonidine* (chemical formula $C^{18} H^{10} NO$), obtained from it in colourless prisms, and of the composition and properties of citrate of quinine. (*See* p. 31.)

The same gentleman also announced the discovery of lactic acid in vegetables, especially in the peduncles of *Solanum Dulcamara*, and in the liquid which dropped from freshly-cut vine-branches. He likewise mentioned that he had obtained salicylous acid by distilling with water the boughs of *Populus balsamifera*.

Prof. Hlasiwetz read a paper on certain substances produced by the decomposition of parabanic acid. This able chemist had tried to obtain cholestrophane, $C^{10} H^6 N^2 O^6$, by the substitution of the hydrogen in parabanic acid, $C^6 H^2 N^2 O^6$, by $C^4 H^4$, $C^4 H^5$, &c. He obtained by these means an organic periodide of the empirical formula $C^{18} H^{17} NO^{10} I^2$. The rational formula for this combination could be obtained by its decomposition; Prof. Hlasiwetz, however, preferred the empirical one, as explaining better the different position of the iodine atoms.

Dr. Lerch communicated the results of his researches on chelidonic acid and chelidonates, and the substances obtained by the decomposition of both. He obtained, by the protracted action of ammonia, an amine acid, named by him *chelidaminic acid* (formula 3HO, $C^{14} H^5 NO^8$), which, when decomposed under the influence of an elevated temperature, gave an aminic base (formula $C^{10} H^5 NO^4$, 2HO). He concluded with a detailed account of the substances produced by dry distillation and by the action of chlorine.

September 18.

Dr. Lerch discussed the nature of rhodizonic acid and of carbonic-oxide potassium. This last substance is a mechanical aggregate, constant in dry air, instantly changed by contact with atmospheric moisture; when treated with hydrochloric acid, it gives (according to circumstances) four differently composed varieties of rhodizonic acid:—

1. $C^{12} H^6 O^{12}$.
2. $C^{12} H^5 O^{12}$.
3. $C^{12} H^7 O^{15}$.
4. $C^{12} H^5 O^{14}$.

Saline combinations could only be obtained with variety 4.

Dr. Lerch also stated, that in continuing Prof. Engel's researches on the soluble portions of the human cerebral substance, he had found among them chloride of sodium, creatine, and uric acid.

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M. Göttl exhibited objects obtained by separating the solid deposit (sinter) from the "Sprudel" water, and stated that, according to his estimate, more than 1,000,000 lbs. of this substance might be brought into the market in various shapes. The sinter is affected by light, which gives it various tints. Qualitative analysis has proved it to contain nickel, cobalt, and chromium.

September 20.

Prof. Fresenius read a paper on the method of analysing and bottling for export chalybeate and sulphuretted mineral waters. He proposed to determine at the spring itself the iron and sulphur contained in the waters, by testing them with permanganate of potash and solution of iodine, a method which he had found to give very exact results.

Prof. Fresenius gave some further and shorter communications, on the alteration of chloride of calcium when exposed to a boiling temperature; on chromate of copper; on a new test for antimony; on the determination of copper by means of zinc: he also exhibited several chemical apparatus, as a water-bath with constant level; a pneumatic trough, and an apparatus to get rid of chlorine and other noxious gases, when they accumulate in chemical laboratories or lecture rooms.

Dr. Beigel announced that he had found, by microscopical investigation, particles of mercury in the gall-stones, which he had treated for cholesterine.

Dr. Lamatsch remarked, with reference to Dr. Beigel's communication, that he and Dr. Kletzinsky had discovered the presence of mercury in the urine of syphilitic patients who had been treated with mercurial preparations a long time before the experiment.

Prof. Böttger showed experimentally his method of discovering small quantities of diabetic sugar in urine. The liquid to be heated is boiled for a short time with a solution of carbonate of soda and basic nitrate of bismuth. The presence of diabetic sugar is made manifest by the liquid becoming of a gray or black tint, originating from the reduction of the bismuth.

The same chemist also exhibited a specimen of artificial marble, made at Hamburg, which he supposed to be a combination of sawdust, a solution of an alkaline silicate (*Wasserglas*), and some metallic oxide.

Dr. Lamatsch also announced that he had succeeded in preparing considerable quantities of fruit-æther, pepsine, and parigline. The largest proportion (2 per cent.) of the last substance was obtained from Mexican sarsaparilla.

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THE CHEMICAL GAZETTE.

No. CCCXLVI.—March 16, 1857.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On some Compounds of Vanadic Acid. *By* KARL VON HAUER.

WE are indebted to the exertions of Patera for rendering vanadium accessible to chemists. Von Hauer has already commenced an investigation upon the compounds of vanadium with material obtained by the process described in our last Number.

The analysis of the vanadiates is attended with many difficulties, as we possess no single perfect precipitant for any of the oxides of this metal. And even if we give up the direct determination of the acid, there is no known method by which the base can be obtained perfectly free from vanadium. This is especially the case in the separation of the alkalies from vanadic acid.

Neither the oxide nor the acid is precipitable by sulphuretted hydrogen.

If the solution of a bivanadiate be reduced by oxalic acid at a boiling heat, and the blue solution be then mixed with ammonia, the oxide is certainly thrown down; but in the subsequent filtration, notwithstanding every precaution, a small quantity always becomes oxidized, and the filtrate, although colourless, always contains some vanadium, even when the precipitate is washed with water containing ammonia, with muriate of ammonia or alcohol.

If the solution of a bivanadiate be mixed with hydrosulphate of ammonia, and then decomposed by a dilute acid, only a part of the vanadium is thrown down as sulphuret, while a portion is reduced to oxide, and the fluid standing over the precipitate appears blue.

The suboxide of vanadium (VO) was characterized by Berzelius as resisting entirely the action of acids; it is easily obtained when the oxide or the acid is heated in a current of hydrogen gas. The author consequently tried the ignition of the alkaline salts of vanadic acid in a current of hydrogen, and treated the residuary black mass with dilute acetic acid. But it turned out that when in combination with bases, the whole quantity of acid is never convertible into suboxide; only a portion remained undissolved, whilst the solution, by its slight blue colour, indicated the presence of a small quantity of oxide (VO^2), which obstinately resisted reduction however long the ignition in hydrogen gas was continued. A somewhat more favourable result is obtained when the alkali

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bivanadiate is freed from water by heat, then powdered, mixed with finely-divided charcoal, and ignited in hydrogen gas. This method of separation will be found pretty exact, the quantity of oxide remaining, which then dissolves as vanadite of the alkali, being very small, but it is attended with the disadvantage that the heated mass adheres so firmly to the tray that it can hardly be separated from it entirely.

If the solution of a bivanadiate be mixed with a neutral solution of perchloride of mercury, no precipitate is produced, but on the addition of ammonia a very voluminous yellow precipitate is thrown down; this appears to be insoluble in alcohol, as even after long washing therewith the filtrate remains perfectly colourless. Nevertheless when the filtrate is evaporated to dryness, it is found to contain vanadium. The same is the case when the solution of a bivanadiate is precipitated with protonitrate of mercury, and the precipitate washed with a dilute solution of the latter salt. In this case also the filtrate appears colourless, but yet it contains some vanadium. Vanadic acid is also pretty completely thrown down by solution of nitrate of silver, and the purple-red precipitate formed is insoluble in alcohol. If the precipitate obtained by the agency of mercurial salts be calcined, the quantity of vanadic acid obtained is always much too little; the loss usually amounts to several parts per cent.

The limited quantity of material did not allow it to be ascertained exactly whether much was carried off mechanically by the volatilization of the mercury. This must remain to be determined by subsequent investigations.

The bivanadiates, however, require peculiarly exact analyses in order to ascertain their chemical constitution, in the first place because they all contain much water, and in the second on account of the high equivalent of the acid in comparison with those of water and base. The only properties of vanadic acid which proved to be really adapted for the purposes of analysis were the following. The insolubility of the vanadiate or bivanadiate of ammonia in a solution of muriate of ammonia and alcohol. The insolubility of the bivanadiate of soda in alcohol. The precipitation of this compound by strong alcohol is very complete, and is only attended with the single disadvantage, that a part of the precipitate is deposited so firmly upon the glass that it can only be washed off with difficulty. Lastly, the decomposition by fusion with an alkaline carbonate of those salts which contain a base the carbonate of which is insoluble in water.

The mode of employment of these properties in the analyses will be more exactly explained with reference to the analysis of the particular salts.

Bivanadiate of Ammonia, $NH^4O, 2VO^3+4HO$.—The neutral vanadiate of ammonia received from Patera was dissolved in boiling water, by which some impurities, such as oxide of uranium, silica, &c., were left behind. The filtered fluid was concentrated by evaporation, and during this operation concentrated acetic acid was added in small portions, in accordance with the directions of Berze-

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lius, until the red colour of the solution produced thereby no longer increased in intensity. When the hot solutions of vanadiates are mixed with acetic acid, they are all coloured immediately by the formation of a salt containing a larger quantity of acid; the colour varies from pale yellow to blood-red according to the concentration of the fluid. When the quantity of acid added is not sufficient, the coloration often disappears again during the boiling, but reappears again and becomes permanent on a second addition. This, however, only applies to acetic acid. If these solutions be mixed with sulphuric or muriatic acid, the coloration frequently disappears again on boiling, even in the presence of a considerable excess of the acid; an observation which was made by Berzelius. The dry salts also exhibit the same reaction when an acid is poured over them; the colourless ones become yellow, and the yellow ones dark red. This is consequently an excellent means of testing the precipitates obtained in the analyses, or substances otherwise separated, to see whether they contain vanadic acid. The colouring power of the acid salts is very considerable, and in this way very small quantities of vanadic acid may be detected. The solutions of the bivanadiates of ammonia and soda exhibit the most intense red coloration, and their colouring power is therefore the greatest. The production of a true precipitate by the addition of acetic acid to vanadiates, as described by Berzelius, was never observed by the author, even when the fluid was very concentrated. At the spot where the acetic acid is added, the yellow or red colour is suddenly produced, and this, when it is not stirred, only becomes diffused gradually, just as in the neutral chromates under the same circumstances.

After the cooling of the concentrated fluid, the bivanadiate of ammonia shoots out in reddish-yellow crystals of the size of an oat-grain, which however exhibit very indistinct forms. Better developed individual crystals are obtained by the spontaneous evaporation of the solution. It must be mentioned, however, and this applies to all the other salts of this series, that the crystallizing dishes must be protected by coverings of filtering-paper from the dust, as this always causes the formation of oxide by reduction, by which the crystals obtained are contaminated. The best plan is to allow the solutions to evaporate under a bell-glass over sulphuric acid. The bivanadiate of ammonia is stable in the air. Analysis:—

NH^3	6·00	1 =	17	6·87
VO^3	75·46	2	185·2	74·91
HO	18·54	5	45	18·20

Bivanadiate of Soda, $NaO, 2VO^3 + 9HO$.—This salt is easily prepared. Vanadic acid free from oxide is mixed with carbonate of soda and fused. Soda is added so as to produce neutral vanadiate of soda. If the vanadic acid is not free from oxide or suboxide, which is frequently the case when in preparing it from vanadiate of ammonia the latter has not been heated with sufficient care, it is fused in equal proportions with nitrate of soda. It is necessary to take such a quantity of the soda-salt that neutral vanadiate of soda

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may be first produced, because this is readily soluble without decomposition in water. The anhydrous bivanadiate, on the contrary, is difficult of solution in water, and does not dissolve without decomposition; even when hot water is poured over it, there always remains a quantity of a very acid salt in the form of an insoluble residue. The aqueous solution is treated in the same way as in the preparation of bivanadiate of ammonia; it is evaporated and mixed with concentrated acetic acid until the fluid acquires a red colour. It is necessary to add the acetic acid gradually and in small portions, in order to avoid too great an excess of it, as otherwise a great deal of vanadic acid is deposited in the form of dark red crusts upon the walls of the vessel during the evaporation. On cooling, the bivanadiate of soda shoots into large, bright red, shining crystals, resembling protacetate of manganese in their form, but with this difference, the apices of the rhombic prisms are not truncated. To free the crystals obtained completely from adherent acetate or nitrate of soda, they are again dissolved in water. The solution takes place easily and without decomposition in cold water. The solution is again evaporated and left to cool, or left to spontaneous evaporation; in the latter case particularly fine crystals are obtained. If hot water be poured over the crystals, a partial decomposition takes place by the separation of an acid salt, which remains as a dark red, difficultly soluble residue. The same decomposition takes place when the crystals are thrown into cold water, and this is rapidly heated before the crystals are dissolved.

The salt effloresces on the surface in dry air, and becomes dull and yellow. The crystals are therefore dried for a short time on bibulous paper, and preserved in a well-closed vessel which has been breathed into; they may then be preserved without change. Analysis:—

NaO	10·11	1	= 31	10·43
VO^3	61·69	2	185·2	62·31
HO	27·72	9	81	27·25

Bivanadiate of soda dissolves easily and without decomposition in cold water; it may therefore, as above stated, be readily recrystallized. It is scarcely, if at all, soluble in strong alcohol.

The salt, deprived of water at a moderate heat, retains its crystalline form, and possesses a rusty-brown colour. At the commencement of ignition it fuses with ease, and solidifies on cooling to form a blackish-red, non-crystalline, varnish-like, shining mass. The anhydrous salt is but slightly soluble even in boiling water; on the addition of an acid, however, it dissolves readily. When boiled with water containing oxalic acid, it dissolves completely, with evolution of carbonic acid, and the vanadic acid is reduced to oxide. The solution first of all becomes green, from the formation of an intermediate oxide (a mixture of acid and oxide), then blue by complete reduction to oxide. This is the best means of cleaning the crucible from the firmly-adherent mass of fused bivanadiate.

If nitric acid be gradually added to the boiling solution of the

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blue fluid reduced by oxalic acid, the fluid again becomes green and retains this colour however long it may be heated, and even after the addition of an excess of nitric acid. This behaviour towards nitric and oxalic acids is exhibited by all bivanadiates, and it appears to show that the green oxide is a definite grade of oxidation, and not a mere mixture of acid and oxide.

The author repeatedly mentions that the colouring power of bivanadiate of soda is particularly strong; to measure its intensity approximatively, the following experiment was made. 96 milligrms. of the crystallized salt were dissolved in ½ a litre of water. Of this solution, which was of a strong yellow colour, 100 cub. centims. were gradually diluted to a volume of 3 litres. Even this solution still presented a distinct yellow colour. But 96 milligrms. of the crystallized salt contain 70 milligrms. of dry bivanadiate of soda; consequently 1 part of this dissolved in 214,000 parts of water, still gave a distinctly visible yellow colour.

The author did not obtain a potash-compound corresponding with the bivanadiate of soda.

According to Berzelius, the bivanadiate of potash has a composition agreeing with the formula $KaO, 2VO^3 + 3HO$. He gives three methods for its preparation, of which the following is said to be the best. To the nearly boiling solution of neutral vanadiate of potash, concentrated acetic acid is gradually added in small quantities; the concentrated fluid is precipitated by alcohol, the precipitate washed with alcohol, dissolved in boiling water, and allowed to cool and crystallize. By this process the author obtained salts containing very different amounts of water. The small quantity of material at his command prevented his following the subject any further.

Vanadic Acid with Baryta.—According to Berzelius, bivanadiate of baryta is obtained when the clear aqueous mixture of bivanadiate of potash and muriate of baryta is left to evaporate spontaneously, or mixed with alcohol until it just begins to grow turbid. The author mixed a very dilute solution of the potash-salt, prepared according to the above prescription of Berzelius, with some chloride of barium, and left the solution to spontaneous evaporation. Well-developed crystals were deposited, but their composition did not correspond with that of a bivanadiate of baryta. In numerous analyses, made with crystals derived from repeated preparations, the results always showed that this salt only contains 5 equivs. of vanadic acid to 3 equivs. of baryta.

As the compounds of vanadic acid with baryta are very slightly soluble in water, a very dilute solution of the potash-salt must be employed, as otherwise a precipitate in the form of a yellow powder is immediately produced. To this dilute hot solution, chloride of barium is added in drops, and in case a precipitate is produced, also a little acetic acid, the presence of which considerably increases the solubility of the salt. By this means therefore the precipitate formed is entirely or partially dissolved; in the latter case it is filtered, and the filtrate left to evaporate spontaneously in a dish covered with filtering-paper. On cooling, crystals are immediately deposited, and

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these attain a diameter of several millimetres by standing for some weeks under the mother-liquor. The salt forms shining, reddish-yellow, obliquely-prismatic crystals. Analysis:—

BaO	26·39	3	= 229·5	26·57
VO^5	53·76	5	463	53·61
HO	19·85	19	171	19·80

This salt is consequently $\frac{5}{3}$ vanadiate of baryta, in accordance with the formula

$$3BaO, 5VO^5 + 19HO,$$

or if we regard it as a compound of neutral and acid vanadiate of baryta,

$$BaO, VO^5 + 2(BaO, 2VO^5) + 19HO.$$

Bivanadiate of Strontia, $SrO, 2VO^5 + 9HO$.—If the solution of an alkaline bivanadiate be mixed with a solution of chloride of strontium, no precipitate is produced; the compounds of strontia with vanadic acid are therefore much more soluble than those of baryta. For the preparation of the salt, a strongly-concentrated hot solution of bivanadiate of soda was mixed with chloride of strontium. After cooling, red crystals were deposited; they exhibited the form of the bivanadiate of soda. They are unalterable both by moist and dry air. Analysis:—

SrO	16·51	1	= 51·8	16·29
VO^5	58·70	2	185·2	58·23
HO	24·79	9	81	25·47

When heated, this compound behaves exactly like that of baryta. The salt is certainly much more soluble than the baryta-salt, but still requires a considerable volume of water in comparison with that in which it was originally contained. When the crystals are treated for a long time with cold or hot water, a decomposition always takes place gradually; a yellow insoluble residue is left.

Besides the salt here referred to, the author obtained a second strontia compound in large crystals of remarkable beauty, which showed a higher amount of water, and also appeared to have a different composition in other respects.—*Sitzungsber. der Akad. der Wiss. zu Wien*, xxi. p. 333.

On Conhydrine, a new Alkaloid from Conium maculatum.

By Prof. T. Wertheim.

If the fresh flowers of *Conium maculatum* be extracted with hot water containing sulphuric acid, and the moderately-concentrated extract, after supersaturation with caustic lime or potash, be submitted to as rapid a distillation as possible, a strongly alkaline distillate is obtained, which, besides ammonia and coniine, contains a hitherto undescribed organic base. It is obtained in the pure state in the following way.

The alkaline distillate is neutralized with sulphuric acid, the fluid evaporated on the water-bath to the strongest syrupy consistence,

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the residue extracted with very highly rectified alcohol, and the alcoholic solution separated by filtration from the deposited sulphate of ammonia. After the alcohol added has been distilled off in the water-bath, the residue is gradually mixed, with continual refrigeration, with a considerable excess of the most concentrated solution of potash; the mixture, when completely cold, is then brought in contact with a sufficient quantity of pure æther, and left so for a long time with frequent agitation; the ætherial solution, which is of a yellowish or brownish-red colour, is drawn off from the potash solution beneath it, and the æther distilled off as completely as possible in a glass retort on the water-bath; the remaining fluid is afterwards put into a tubulated retort of smaller dimensions, and the distillation continued on the oil-bath in a current of hydrogen gas, the heat being very gradually increased. In this way oleaginous coniine first distils over, contaminated at the commencement with a little æther and water, but afterwards far purer and perfectly colourless; but when the heat is gradually raised, the retort becomes filled with beautiful, colourless, splendidly-iridescent, crystalline laminæ, which appeared in one case at 302° F., in another at 374° F., and in a third only at 410° F. They appear sooner the more slowly the preliminary stage of the distillation is conducted. In the first case this was done very slowly, so that the coniine was evaporated at the lowest possible temperature.

Of course, in this mode of preparation, a considerable contamination with coniine cannot be avoided. But the greater part of this may be easily got rid of merely by pressing the crystals; for this purpose the sublimed crystalline crust is detached from the neck of the retort, and put into a glass vessel which is immersed in a freezing mixture; by this means the crystals are rendered more compact, whilst at the same time their mass increases, because the coniine passing over with them contains a considerable quantity of the substance in solution; they are then pressed strongly between Swedish filtering-paper, and finally purified completely by repeated recrystallization from æther. The substance thus purified, when completely dried under the air-pump, forms perfectly colourless, nacreous, iridescent, crystalline laminæ, of a coniine-like odour. Five Vienna hundredweights=280 kilogrms. of freshly collected flowers, when treated as above described, gave 17 grms. of pure crystals; but even perfectly ripe seeds furnished it in considerable quantity together with the ordinary coniine, and it must be left undecided for the present whether the quantity in the ripe seeds is essentially less than in the fresh flowers. The latter were collected in the immediate vicinity of Pesth and Ofen, and the ripe seeds in the neighbourhood of Stuhlweissenburg.

The investigation of this crystallized substance furnished the following facts. It fuses when slightly heated, and may be gradually sublimed even below 212° F. At higher temperatures it volatilizes rapidly and without residue, diffusing to great distances the peculiar odour of coniine, or one very nearly allied to it. It is tolerably soluble in water, and readily soluble in æther and alcohol; the solu-

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tion has a strong alkaline reaction. Even at the ordinary temperature it expels ammonia from its compounds, but it appears to be separated from its salts by coniine; its aqueous, alcoholic, or ætherial solution, neutralized with muriatic acid, furnished no crystals either by slow or rapid evaporation; but when the alcoholic solution, neutralized with muriatic acid, was mixed with alcoholic solution of perchloride of platinum, taking care that the latter should not be in excess, and this mixture was left first of all *in vacuo* over sulphuric acid, and as soon as crystals began to be formed at the edge, placed to evaporate in the air, remarkably beautiful, large, hyacinth-red crystals were obtained, which were determined by Prof. Peters. The forms of this platinum-salt belong to the dimetric system; it gave on analysis—

C	27·59	27·34	27·80	16	27·47
H	5·30	5·48	5·16	17	5·15
N	4·55	..	..	1	4·01
Pt	27·95	27·99	28·04	1	28·33
Cl	..	..	..	3	30·47
O	..	..	..	2	4·57

The base which is contained in this platinum-salt consequently has the formula $C^{16} H^{17} NO^2$. Thus we have

Coniine ..... $C^{16} H^{15} N$
New base..... $C^{16} H^{15} N, H^2 O^2$.

The latter therefore only differs from coniine by the elements of water, for which reason the author calls the new base *conhydrine*.

By distillation with anhydrous phosphoric acid, it loses this elementary group of 2 equivs. water, and furnishes coniine, which is exactly similar to the ordinary coniine in all its properties, and even in its action upon the animal organism; whilst conhydrine certainly produces the same phænomena of poisoning, but in a far weaker degree.

The author takes the opportunity of making the following observation upon the muriate of coniine. In the chemical handbooks it is stated that muriate of coniine crystallizes with difficulty, and that the crystals are deliquescent; this, however, is by no means the case; any quantity, however small, of coniine, brought in contact with muriatic acid upon a watch-glass, furnishes a corresponding quantity of crystals in a very short time; these crystals are not in the least deliquescent, and when a rather large quantity is prepared, they are easily obtained very regular in form and of considerable size. The crystals are rhombic, and have the formula $C^{16} H^{15} N$, HCl.

Between coniine and conhydrine we find a connexion which renders it interesting to compare these two bases with quinine and Wittstein's new base cinchonidine.

Thus if ordinary quinine $= C^{20} H^{12} NO^2$ be treated with anhydrous phosphoric acid, phosphate of quinoiline and a gas are obtained; the gas is absorbed in small quantity by water, burns with a pale yellow colour, and is taken up in very large quantity by sulphuric

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acid, in the manner of the gaseous hydrocarbons, which are prepared from the alcohols by the elimination of water. This decomposition may therefore probably be represented by the following equation:—

$$C^{20}\,H^{12}\,NO^2 + PO^5 = PO^5, HO, C^{18}\,H^8\,N + (C^2\,H^2).$$

Wittstein's cinchonidine has the formula $C^{18}\,H^{10}\,NO^2$, and is consequently to be regarded as a homologue of ordinary quinine less $C^2\,H^2$.

The result of the action of anhydrous phosphoric acid upon this quinine may, however, almost be predicted with certainty from the above premises; the reaction will evidently take place in accordance with the equation

$$C^{18}\,H^{10}\,NO^2 + PO^5 = PO^5, HO, HO, C^{18}\,H^8\,N,$$

and will therefore present the most complete analogy with the similar reaction of conhydrine.—*Sitzungsber. der Akad. der Wiss. zu Wien*, xxii. p. 113.

On Teriodide of Bismuth. By R. Schneider.

The teriodide of bismuth, which had hitherto only been prepared in the humid way, may be obtained with ease and certainty in the dry way, by heating an intimate mixture of 1 equiv. (32 parts) of tersulphuret of bismuth and 3 equivs. (47·5 parts) of iodine in a spacious, loosely-covered glass flask. The mass fuses even at a moderate temperature with the loss of a little iodine; when the temperature is raised, it boils and gives off reddish-brown vapours, which condense in the colder parts of the flask, forming shining crystalline laminæ of iodide of bismuth. In this case a simple displacement of the sulphur by the iodine appears to take place; for if the mixture of sulphuret of bismuth and iodine be exposed to a gradually increased temperature in the absence of air (in an atmosphere of carbonic acid gas), it may be perceived that the sulphur sublimes before the iodide of bismuth. If it be rapidly heated, and atmospheric air be present in the flask, the greater part of the sulphur is converted into sulphurous acid; a small portion is transformed into iodide of sulphur.

The sublimate obtained may be completely freed from any adherent iodine by heating in the water-bath. It is then pure iodide of bismuth, exactly agreeing in its composition with oxide of bismuth.

This iodide of bismuth prepared in the dry way is a substance of remarkable beauty. It forms large, thin, black, crystalline laminæ, with a very brilliant metallic lustre; their form may be distinctly recognized as a regular 6-sided prism. When heated with free access of air, it is for the most part volatilized in brown vapours, leaving a little basic iodide of bismuth of a reddish-brown colour. It is not perceptibly altered by cold water; when boiled with water it is converted into a basic iodide of bismuth. The aqueous solutions of caustic alkalies decompose it even in the cold, but still more

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rapidly when heated; oxide of bismuth is separated. Alkaline sulphurets also rapidly and easily decompose the compound with separation of sulphuret of bismuth, which retains the crystalline form of the original substance.—*Bericht der Akad. der Wiss. zu Berlin*, 1856, p. 469.

On a peculiar Decomposition of the Sulphite of Ammonia. *By* Dr. F. Rochleder.

Three years ago several pounds of commercial carbonate of ammonia were dissolved in the smallest possible quantity of water and treated with a current of sulphurous acid. The sulphurous acid was evolved from a mixture of charcoal and sulphuric acid. The solution of carbonate of ammonia was exposed to the action of the sulphurous acid until there was no longer any effervescence of carbonic acid, and the fluid had a strong odour of sulphurous acid. The fluid thus prepared was preserved in a glass flask, closed with a cork and secured by a cap of vulcanized india-rubber. During the first two years the fluid presented no alteration, although the vessel was opened three times to take out a part of its contents. In the third year the flask was opened five times for the same purpose. It was never exposed to the action of direct sunlight, but only to that of diffused daylight. The temperature varied between 0° and 72° F. During the last two months a pale yellow precipitate was deposited at the bottom and on the walls of the vessel. According to Payr's examination of this, it consisted of pure sulphur. The filtered fluid contained sulphate of ammonia, small quantities of undecomposed sulphite of ammonia, and some hyposulphurous acid. When exposed to the air the fluid became turbid; when heated, it rapidly became milky by the separation of sulphur. The fluid smelt strongly of sulphurous acid.

From these data, ascertained by Payr, it appears that the following decomposition had taken place. A portion of the sulphurous acid had given off oxygen, and indeed the half of its oxygen, to the other half of the sulphurous acid. By this means from $2S^2O^4$ there was produced $S^2O^6 + S^2O^2$, or sulphuric and hyposulphurous acids. As the acid sulphite of ammonia was converted half into acid sulphate and half into acid hyposulphite, neutral sulphate of ammonia and free hyposulphurous acid must have been produced therefrom, but the latter must have been decomposed into sulphurous acid and sulphur. A bottle filled with the same solution, which in the case described had undergone spontaneous decomposition, was preserved in a dark place for three years without being opened. It had not undergone the least alteration. The oxidation of the sulphurous acid, which had commenced at the expense of the oxygen of the air in the vessel which was repeatedly opened, was continued after the vessel was closed at the expense of the oxygen of a portion of the sulphurous acid.—*Sitzungsber. der Akad. der Wiss. zu Wien*, vol. xxii. p. 289.

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On a peculiar Mode of Production of Nitrous Acid.
By Professor SCHÖNBEIN.

At ordinary temperatures, oxygen, whether contained in the air or prepared in the laboratory, behaves quite indifferently both towards gaseous and aqueous ammonia; whilst, according to the author's previous experiments, the same oxygen, after it has been exposed to the influence of electricity or phosphorus (that is to say, become ozonized), oxidizes both the constituents of ammonia, forming water with the hydrogen, and nitric acid with the nitrogen; hence ozonized oxygen produces nitrate of ammonia with ammonia.

The circumstance that oxygen, under the influence of contact with platinum, produces even in the cold a series of actions of oxidation which it is incapable of producing alone under otherwise similar conditions, led the author to suppose that by the assistance of platinum the ordinary oxygen might also cause the oxidation of the elements of ammonia at a low temperature, and the following statements will show that this is actually the case.

If platinum black moistened with aqueous ammonia be placed in oxygen gas or atmospheric air, and the metallic powder be extracted with distilled water after the substances have stood for some time in contact, this fluid contains nitrite of ammonia, as appears even from the simple fact, that on the addition of dilute sulphuric acid, phosphoric acid, &c. to this aqueous extract, it instantaneously gives the deepest blue tint to starch-paste containing iodide of potassium. Even if the platinum black moistened with aqueous ammonia has only been in contact with oxygen gas or atmospheric air for a minute, so much nitrite of ammonia has been produced even in this short time that its presence may be instantly proved by the above means. The longer the contact, the greater is the quantity of nitrite formed.

At the same time the author also remarks, that, according to his observations, there is no more sensitive reagent for the nitrite than dilute starch-paste mixed with some iodide of potassium; this salt, however, must of course be perfectly free from iodate. Even if the fluid to be tested only contains traces of nitrite of ammonia, soda, or potash, &c., it will immediately communicate the strongest blue colour to the solution of starch and iodide of potassium on the addition of dilute sulphuric acid, a reaction which the nitrates of the same bases do not produce. The author also observes that the slightly acidulated solutions of nitrite of ammonia, &c. immediately give a blue colour to fresh tincture of guaiacum, which is not the case with solutions of the nitrates under the same circumstances.

Dense platinum does not act perceptibly upon oxygen and ammonia at ordinary temperatures, but with the aid of heat considerable quantities of nitrite of ammonia are instantly obtained by means of platinum wire; this is most conveniently done in the following way:—If the extremity of a rather thick platinum wire twisted into a spiral be heated and introduced into a bottle containing air, previously rinsed out with strong liquid ammonia, and a strip of paper coated with acidulated starch-paste containing iodide of potassium

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be held over the spiral, the latter will instantly become deep blue in consequence of the formation of nitrite of ammonia under these circumstances. In the vessel whitish clouds are soon seen to make their appearance during the presence of the heated platinum wire; these are due to nitrite of ammonia; for if they be taken up by a little distilled water, this immediately gives a very deep blue colour to acidulated starch-paste and iodide of potassium, even when the heated spiral has only been allowed to remain a few seconds in the bottle. By the repeated introduction of the heated spiral into a somewhat larger vessel, the bottom of which is covered with strong aqueous ammonia which is frequently shaken up, so much nitrite may soon be accumulated in this fluid, that all the other reactions belonging to this salt may be produced with it.

The temperature at which platinum wire induces the formation of nitrite is below a red heat, as appears from the fact that a heated spiral which no longer exhibits any incandescence even in complete darkness, is still capable of causing the formation of nitrite. It must also be mentioned that iron and copper wires also produce the above-mentioned action, but for this purpose they must be brought to a strong red heat.

It is remarkable that copper, like platinum, is capable, even at ordinary temperatures, of causing oxygen to produce nitrite with ammonia; the following statements leave no doubt on this point. If 50 grms. of finely-divided copper, such as is obtained by the reduction of oxide of copper with hydrogen, be moistened with strong ammonia in a bottle containing oxygen or air, the metallic powder soon becomes considerably heated, and whitish clouds make their appearance in the covered or closed vessel: these are nothing but nitrite of ammonia, as may be easily ascertained by the following means:—If a strip of paper coated with acidulated starch-paste and iodide of potassium be introduced into the vessel which contains these clouds, this rapidly acquires a blue colour; if the same vessel be covered only for a short time with a moistened glass plate (or a watch-glass), the inner side of this will give a deep blue colour to starch-paste containing iodide of potassium and acidulated with sulphuric acid; or if strips of filtering-paper moistened with water be suspended in it, even after the above-mentioned clouds have disappeared and the copper powder has become cool, they will soon take up so much nitrite of ammonia that their aqueous extract produces the same reaction very strongly.

If finely-divided copper moistened with aqueous ammonia be placed in a bottle filled with oxygen gas, and the vessel be closed air-tight, a disappearance of gas takes place by agitation, as is seen from the fact, that when the bottle is opened under water the fluid flows into it and the vessel is entirely or partially filled with it, according to the length of time its contents have been agitated, and the larger or smaller quantity of copper employed.

If atmospheric air be employed instead of pure oxygen, its oxygen is of course taken up, and indeed so rapidly that a moderately large volume of air may be completely deprived of its oxygen in a few

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minutes. Thus if 5 grms. of pulverulent copper be put into a graduated tube of 42 cubic inches filled with atmospheric acid, and so much (rather weak) liquid ammonia be poured in that 35 cubic inches of air still remain in the tube, the contents of the closed vessel need only be shaken briskly for a few minutes in order that, when it is opened under water, this fluid should flow in to the extent of 7 cubic inches. By the employment of sufficient quantities of copper, the author has even extracted all the oxygen from 1 cubic foot of air in a few minutes. As a matter of course, burning bodies are instantaneously extinguished in the residue of the air thus treated, that is to say, the latter behaves like nitrogen; and it is hardly necessary to state expressly that the aqueous ammonia employed in these experiments rapidly acquires a deep azure-blue colour.

From the great comparative rapidity with which the oxygen is taken up by the copper and ammonia under the above-mentioned circumstances, these substances might serve for the preparation of large quantities of nitrogen from atmospheric air, and also for eudiometric purposes.

The azure-blue fluid above mentioned is by no means only a solution of oxide of copper and ammonia, but it also contains nitrite of ammonia, as might be expected from the above statements, and as will be proved by what follows.

If this fluid be mixed with some solution of soda and the mixture allowed to boil for some time, black oxide of copper separates, and on filtration a somewhat yellowish fluid is obtained; this, on the addition of dilute sulphuric acid, communicates the deepest blue colour to starch-paste and iodide of potassium. When evaporated to dryness it leaves a yellowish-white residue, still retaining a slight alkaline reaction; this detonates when mixed with powdered charcoal and heated, and when poured over with sulphuric acid evolves vapours of hyponitric acid and nitric oxide gas. (H. Rose remarks upon this, that Professor Wöhler told him, in the course of last summer, that one of his scholars had evolved reddish-brown fumes from the blue fluid obtained by the exposure of copper-filings and aqueous ammonia to the air, by the addition of sulphuric acid, but that he had not followed the matter any further.) Of course an aqueous solution of this residue, acidified with sulphuric acid, gives a blue colour both to starch-paste containing iodide of potassium and to fresh tincture of guaiacum. These reactions leave no doubt that a nitrite is contained in this residue; this can only be nitrite of soda; and we may therefore conclude, that besides oxide of copper and ammonia, the blue fluid contains nitrite of ammonia, which is decomposed on the addition of soda, forming nitrite of soda and setting free ammonia.

From the preceding facts it appears, therefore, that under the influence of contact of finely-divided platinum and copper, ordinary oxygen is rendered capable of oxidizing the elements of ammonia even at ordinary temperatures, forming water with the hydrogen, and nitrous acid with the nitrogen; the nitrous acid combines with the remaining ammonia to form a nitrite.

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The author hopes on some other opportunity to answer the question why, under these circumstances, nitrous acid or a nitrite is formed instead of nitric acid or a nitrate.—*Bericht der Akad. der Wiss. zu Berlin*, 1856, p. 580.

Observations on Rock Salt. By M. Margueritte.

It is well known that when salt is fused, it crystallizes on cooling in various forms, especially in cubes; these crystals are more or less confused, opake, and always coloured when common salt or crude rock-salt is employed. The results are different when pure salt is calcined, kept in a state of quiet fusion, and cooled slowly; in this crystals are formed, sometimes of considerable volume, and perfectly transparent.

When protected from the air, rock-salt in its native state, that is to say, presenting various gray, red or brown tints, may be fused without decolorization; but if the calcination takes place in contact with the air, and, as in the preceding case, the fusion is tranquil and the refrigeration slow, the earthy matters are deposited at the bottom of the crucible, the chloride of magnesium is spontaneously decomposed in contact with the moist atmosphere, the colouring matters are destroyed under the oxidizing action of the air, and all the impurities are eliminated by the crystallization which takes place in the mass; in this way two very distinct strata, which are easily separated, are formed in the mass. This operation might perhaps be applied with advantage to the purification of crude rock-salt, and also to that of ordinary sea-salt.

The fusion of salt, effected with or without the contact of the air, would explain, up to a certain point, how the salt which is found in the bosom of the earth is contaminated with colouring matters, and how, on the contrary, that which has been exposed to an oxidizing atmosphere is white and transparent.

From these facts we can come to no conclusion as to the origin and formation of rock-salt; for although by fusion we can obtain salt having the aspect, the transparency, and the physical properties of the latter, it is nevertheless certain that the presence of organic remains in the heart of the natural product excludes the probability of its igneous formation; and it would also be difficult to understand how, if a fusion of the mass really took place, the chloride of magnesium was not decomposed. As to the phænomenon of decrepitation, since it is observed to a certain extent in rock-salt as well as in that which has been crystallized in the humid way, it cannot serve as a character in support of the hypothesis of igneous formation.—*Comptes Rendus*, Feb. 16, 1857, p. 348.

Note on the Anomalies presented by Aluminium. By C. Tissier.

Relation between the Density and Alterability.—Hitherto the least oxidizable metals have been amongst the heaviest, such as mercury, silver, gold, and platinum; nevertheless, aluminium, the density of

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which is only 2·56, is the least alterable of all the ordinary metals, after silver, gold, and platinum.

Relation between the Atomic Weight and the Alterability.—In general the metals are more alterable the lower their atomic weight; nevertheless, the atom of aluminium, the alterability of which is so small, only weighs 14; that is to say, it has the lowest atomic weight of all the ordinary metals. It is the half of that of iron, which is 28.

Relation between the Density and the Physical Properties of Metals.—We do not know of any other body of so little density, which possesses like aluminium, the hardness, malleability, tenacity, conductibility, and sonorousness characteristic of what is called a metal.

Aluminium and Thenard's Classification.—According to Sainte-Claire Deville, aluminium does not decompose water*; it should therefore be ranged at least in the fourth section, according to Thenard's classification, and yet its oxide (alumina) is not reducible by hydrogen and carbon, or even by sodium or potassium.

Aluminium does not decompose water, and it decomposes carbonic acid and silicic acid exactly in the same way as potassium or sodium.

What rank must be assigned to Aluminium?—This metal ranks not far from silver in its action upon water and oxygen; near the alkaline metals in its action upon silicic, boracic and carbonic acids, and near iron in its action upon the metallic oxides; in fact, it decomposes all the oxides which are decomposed by iron, except the oxide of zinc. According to this last peculiarity, aluminium would have less affinity for oxygen than iron, and would range beside iron, but below it.

In considering what place aluminium should occupy in the electro-chemical series, we find that it precipitates all the metals from their chlorides up to lead and cadmium inclusive†, so that it comes between cadmium and iron.

To sum up, until chemistry has made further progress, we must not hope to assign aluminium an *exact* place in the classifications. However, as M. Sainte-Claire Deville has said, it will certainly be least out of place by the side of iron. We know, in fact, that at a high temperature iron also decomposes silicic, boracic and carbonic acids; and if aluminium has not the same action upon oxygen and water as iron, it is, as M. Deville has also observed, because we do not know an oxide of aluminium of the formula $R^3 O^4$, an oxide which iron always tends to produce at a high temperature.

Lastly, taking into consideration the electro-chemical properties, it is still in the neighbourhood of iron that aluminium would be placed.

The remarkable properties which distinguish this metal from all others are therefore—

1. Its slight density.

* We admit that it absorbs oxygen from the air at a very high temperature.

† This observation is the result of personal experiments. Aluminium has no action upon the chlorides of iron, zinc, and manganese.

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2. Its resistance to the action of the oxyacids and sulphuretted compounds, which approximates it to gold and platinum.

3. The difficulty with which it enters into alloys, a property which is not shared by the other malleable metals; for iron, zinc, lead, tin, copper, silver, gold, and platinum are capable of forming more or less malleable alloys, whilst aluminium cannot bear more than 10 per cent. of foreign metal, or enter into combination itself in greater proportion, without greatly modifying the ductility of the metal with which it is alloyed.—*Comptes Rendus*, Feb. 16, 1857, p. 350.

Observations on Metallic Phosphurets. *By* H. Hvoslef.

Phosphuret of Iron, Fe^2P, was obtained when the author brought finely-divided iron to a slight red heat in vapour of phosphorus. The iron was reduced from oxide of iron by means of hydrogen. The vapour of phosphorus was carried over the iron by hydrogen, which was passed over boiling phosphorus.

This body is gray, not magnetic, and burns, when heated, with a phosphorous flame. It is not attacked either by muriatic or nitric acid.

Phosphuret of Iron, Fe^6P.—The preceding phosphuret of iron, when exposed to the heat of melting cast iron under a covering of borax, allows phosphorus to escape, and leaves a well-fused regulus, which is of a dark iron-gray colour, very brittle, and has a finely-granular fracture. It is magnetic, and has a specific gravity of 6·28.

Phosphuret of Copper, Cu^4P.—Vapour of phosphorus was produced in a tube closed at one end, and driven over a roll of red-hot copper-leaf. The combination took place with incandescence. The compound is dull gray and caked together.

Phosphuret of Copper, Cu^6P, is obtained when the preceding phosphuret is exposed in a crucible under a cover of borax to the heat of a blast-furnace. It has a rough fracture, is very brittle, and has a specific gravity of 6·59.

Phosphuret of Zinc.—Wöhler first observed, that when a globule of phosphorus salt is heated with metallic zinc before the blowpipe, little flames of phosphuret of zinc burst forth from it. This gave the inducement to the following experiment. Phosphate of soda and ammonia were fused in a crucible to a clear glass; this was powdered and mixed with zinc-filings. The mixture was heated to redness in a luted retort.

After cooling, the retort, when broken, was found to contain a small quantity of a reddish sublimate of fine needles, which burnt in the air with a white luminous flame. When heated without access of air, they became black, but again became red on cooling. When more strongly heated, they lost phosphorus. They are not attacked by acids.

Phosphuret of Zinc, PZn, is contained in the residue, which forms a black cake. It is obtained by extracting this residue with muriatic acid, which removes zinc, phosphate of zinc, and soda. It remains in gray metallic laminæ, which yield a crystalline powder

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with a reddish tinge. It burns in the air with flame, and when heated in a tube gives off phosphorus.

Phosphuret of Zinc, $Zn^3 P$, was obtained when a mixture of 2 equivs. oxide of zinc, 1 equiv. phosphoric acid, and 7 equivs. charcoal were exposed to a strong red heat in a clay retort; carbonic oxide gas, containing phosphorus, which was spontaneously inflammable, was evolved; and after cooling, the neck of the retort contained a dense, here and there crystalline sublimate of dark steel-coloured brittle phosphuret of zinc, which was dissolved by muriatic acid with evolution of a phosphuretted hydrogen gas, which was not spontaneously inflammable and possessed a peculiar odour. Various phosphurets of zinc were obtained by the calcination of oxide of zinc in vapour of phosphorus.

Phosphuret of Zinc and Copper.—When brass was fused with anhydrous phosphoric acid and charcoal-powder under a covering of borax, a well-fused brittle regulus, of a bluish-white colour and laminar crystalline fracture, was obtained. It consisted of 77·54 per cent. of copper, 7·58 per cent. of zinc, and 14·84 per cent. of phosphorus, which comes near the formula $10(Cu^6 P)+Zn^6 P$.—Liebig's *Annalen*, c. p. 99.

On the Preparation of a Writing-ink in Cakes.
By A. Leonhardi.

After the author had discovered the mode of preparation of the so-called alizarine-ink, which is particularly useful, he was anxious to prepare it in a form which would allow it to be sent to a great distance and at any time of the year, render its transport convenient, and diminish its cost considerably, but at the same time fulfil all the requirements of an excellent article. This is attained by the dry alizarine-ink in cakes. The "ink powders" hitherto found in commerce are not to be compared with it, for they not only possess a different composition, but never dissolve completely to form a clear solution in water, and their employment is attended with so many inconveniences and disadvantages, that they have been given up. Common black ink may indeed be evaporated to dryness, but it leaves a residue which does not again dissolve completely in water, and never furnishes a useful ink by this solution. The recipe for the preparation of the cake-ink is as follows:—

42 parts of Aleppo galls and 3 parts of Dutch madder are extracted with a sufficient quantity of hot water; the fluid is then filtered, $5\frac{1}{5}$ parts of sulphate of iron are dissolved in it, and 2 parts of a solution of iron in wood-vinegar, with $1\frac{1}{5}$ part of solution of indigo, are added to it. The mixture is evaporated to dryness at a moderate heat, and formed into cakes of a proper size (for instance 5 inches long, $3\frac{1}{2}$ inches broad, and $\frac{3}{8}$ inch thick).

1 part of this cake-ink dissolved in 6 parts of hot water, furnishes an excellent writing and copying ink, whilst even with 1 part of cake-ink and 10 to 15 parts of water, beautiful writing-inks are obtained.—*Mittheil. des Gewerbevereins für das Königr. Hannover*, 1856, p. 249.

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ANALYTICAL CHEMISTRY.

Note on the Detection of Phosphorus. By L. DUSART.

THE process employed for ascertaining the presence of phosphorus when it is in a free state or under any other form, consists in bringing it to the state of phosphoric acid, and then forming the characteristic precipitates with bases. This method, although easy, requires a considerable quantity of material when the phosphorus is in very small proportion. The process proposed by the author is founded on the property possessed by phosphorus, the phosphurets, and phosphorous and hypophosphorous acids, of furnishing phosphuretted hydrogen gas in the presence of nascent hydrogen.

To the known properties of this gas, the most characteristic of which are the reduction of metallic salts, and especially of nitrate of silver, its alliaceous odour, and the production of white vapours in contact with the air, the author adds one of great delicacy, namely, the emerald-green colour which it communicates to the flame when burnt in an atmosphere of hydrogen. This may be shown in the following manner. A fragment of phosphorus is put between two plugs of asbestos in a glass tube, which is drawn out at one extremity; the gas produced from pure distilled zinc is passed through and ignited. The green colour is immediately perceived at the orifice of issue; this soon disappears when the tube gets heated; if the flame be then crushed under a saucer, the phænomenon reappears on all the part in contact with the porcelain, and disappears again when the temperature is allowed to rise. It may be rendered continuous by adapting a kneed-tube to the apparatus, bent into the form of a V at its lower part which is immersed in the mercury, so that the orifice of issue is on a level with the surface of the metal. If it be then ignited, the extremity of the tube will be cooled by the mercury, and the gas will burn, forming an emerald-green interior cone and a scarcely visible pale blue exterior cone. The same effect is produced when the phosphorus is put into the hydrogen apparatus; but in this case the phosphorus appears to be in the form of gaseous phosphuretted hydrogen, at least when the quantity employed does not exceed 5 or 6 milligrms., or the temperature of the acid liquid does not rise too high. No diminution of intensity in the coloration is observed if the gaseous mixture be passed into a long column of fused potash, of anhydrous lime, and then into a series of tubes kept at 212° F., and containing very finely granulated zinc.

An apparatus of 1 litre in capacity, with 1 milligrm. of phosphorus, and yielding on an average 10 litres per hour, furnished 15 litres of gas presenting a very distinct green coloration. When the phosphorus is divided, like that on matches, the coloration is more intense but a little less durable.

With the paste detached from a match, weighing 1 centigrm., we may see the coloration of the flame, reddish-yellow spots on the

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porcelain, apparently very finely divided phosphorus or solid hydruret of phosphorus, phosphorescence in the dark at the extremity of the issue-tube, and in the bottle when a few bubbles of air are let into it (this is not always free from danger), the white vapours of bubbles set free at the surface of a water-trough, the same vapours in the gas collected under a bell-glass and exposed to the air, and lastly the series of little detonations at the orifice of issue. After the lapse of an hour and a half, the coloration of the flame is still very distinct. Phosphorous and hypophosphorous acids are also reduced by nascent hydrogen, and present all the phænomena observed with phosphorus.

The character furnished by the flame is as delicate as the arsenical spots with Marsh's apparatus, and lasts longer. This coloration is independent of that produced by copper and boracic and muriatic acids; arsenic and antimony whiten the flame.

The peculiar odour of the hydrogen obtained with iron, which has been attributed alternately to a hydruret of iron and to a hydrocarburet, is entirely due to phosphuretted hydrogen. On passing the gas, which burnt with a green flame, produced from iron which contained neither arsenic nor antimony, into a series of tubes containing pumice-stone impregnated with nitrate of silver, the alliaceous odour was replaced by a weak odour of bicarburetted hydrogen gas, and the gas burnt with a scarcely visible blue flame, without a trace of green, and slightly smoky at the point; the nitrate of silver was reduced, and contained some phosphate. By this process the author was able to prove the diminution of the phosphorus in the different commercial irons, from cast iron to pianoforte wire. The gas must be passed over fragments of fused potash to get rid of hydrosulphuric acid.—*Comptes Rendus*, Dec. 15, 1856, p. 1126.

Note on the Quantitative Determination of Chlorine, Bromine, and Iodine. By F. Pisani.

Chlorine.—After the chloride to be analysed has been slightly acidified by pure nitric acid, a known quantity of silver is added to it from a normal solution of nitrate of silver; this should be in slight excess (2 or 3 milligrms.). It is then filtered to separate the chloride of silver, which is carefully washed; the excess of silver is determined in the filtrate, and the difference gives that which is combined with the chlorine, and consequently the chlorine itself. The determination of the silver is effected by means of iodide of starch, which allows the appreciation of the excess of silver employed within $\frac{1}{10}$th milligrm. This mode of determining chlorine gives very exact results, without the necessity of any weighing.

Bromine.—The operation is exactly the same.

Iodine.—Iodine may be determined in the same way as chlorine and bromine, but it is more simple to employ the following means.

A few drops of soluble iodide of starch are added to the liquid containing the iodide to be analysed; the quantity must be suffi-

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cient to give it a distinct blue tint. A normal solution of silver is then dropped in until the iodide of starch is decolorized, which only takes place after the complete precipitation of all the iodine contained in the alkaline iodide. The number of divisions employed is then read off, and the corresponding quantity of iodine is calculated. For more exactness, the quantity of silver which has served to decolorize the iodide of starch may be deducted from the quantity employed; the former quantity may be known beforehand by colouring the liquid to be analysed with $\frac{1}{2}$ cub. cent. of a normal solution of iodide of starch.

Chlorine and Bromine.—These two bodies are precipitated by a known quantity of nitrate of silver in slight excess; the precipitate of chloride and bromide of silver is separated by filtration, washed, and weighed with the greatest care. The excess of silver employed is determined in the filtrate by iodide of starch; the difference gives the quantity of silver combined with the chlorine and bromine within $\frac{1}{10}$th milligrm. From the weight of the chloride and bromide of silver, and the quantity of silver which they contain, the weights of chlorine and bromine in the mixture are calculated.

Bromine and Iodine.—The method is the same.

Chlorine and Iodine.—In this case the same method may be adopted, but by the following process all weighing is dispensed with. A few drops of soluble iodide of starch are added to the mixture of chloride and iodide, and the iodine is determined as above; that is to say, the addition of the normal solution of silver is stopped the moment the iodide of starch is decolorized. The quantity of silver added corresponds exactly to the iodine contained in the mixture; for the iodide of starch loses its colour before the precipitation of the chlorine. To determine this, the solution of silver is poured in until it is in slight excess. After filtration, the excess of silver employed is determined, in order to know what is combined with the chlorine, and from this the quantity of chlorine is calculated. This determination is very quickly effected, and is very exact.

Chlorine, Bromine, and Iodine.—The liquid is divided into two parts, to one of which a known slight excess of silver is added; the precipitate is filtered, washed and weighed, and the excess of silver in the filtrate determined by iodide of starch. The difference gives the quantity of silver combined with the three metalloids.

From the other portion of the liquid the iodine is precipitated by nitrate of palladium; it is then filtered, and the palladium in the filtrate is got rid of. The filtrate then only contains the bromine and chlorine, which are determined as above indicated. In this latter case, however, it is useless to take the weight of the chlorides and bromides of silver, as knowing the iodine by the difference between the weight of the silver combined first with the chlorine, bromine and iodine, and afterwards with the chlorine and bromine, and also the weight of the iodide of silver, it is sufficient to deduct the latter from the weight first obtained to get that of the chlorides and bromides of silver.—*Comptes Rendus*, Feb. 16, 1857, p. 352.

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THE CHEMICAL GAZETTE.

No. CCCXLVII.—April 1, 1857.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Magnesium, its Preparation and Volatilization.
By MM. H. SAINTE-CLAIRE DEVILLE *and* CARON.

THE chemical properties of magnesium have been determined with great perfection by M. Bussy, who discovered this metal, and all the experiments since made have confirmed his results.

One of the physical properties of magnesium, however, has not hitherto been ascertained; it is a new fact which still further approximates zinc and magnesium, and gives them an additional property in common. Magnesium is volatile, like zinc, and nearly at the same temperature. Thirty grammes of it have been distilled with ease in charcoal vessels. When the magnesium is pure it leaves no residue, and the sublimed metal is white and surrounded by a small quantity of oxide. When it is impure, it leaves in the charcoal tray a certain quantity of very light and complex black matter, and the distilled magnesium is covered with little colourless, transparent needles, which are rapidly destroyed with formation of ammonia and magnesia, indicating the probable existence of a nitruret of magnesium analogous to the remarkable bodies already discovered by Wöhler and Rose for a certain number of simple bodies.

Magnesium fuses at a temperature very near that of the fusion of zinc. At a temperature a little higher it ignites, producing a brilliant flame, in the midst of which indigo-blue tufts are seen, especially when a jet of oxygen is thrown upon the fused metal from an oxyhydrogen blowpipe. The combustion of magnesium is accompanied by all the phænomena observed with zinc, denoting a volatile metal, the oxide of which is fixed and infusible: a brilliant flame, a deposition of magnesian flakes and a rapid combustion.

The density of magnesium is 1·75. The malleability and ductility of magnesium, and the dependent physical properties, are still under investigation, as well as its electrical conductibility, which is interesting on account of its extreme lightness. It files very easily and burnishes wonderfully. It resists the air very well, especially when it is pure and its surface is polished; it is therefore comparable in this respect with zinc, which perhaps is a little more resistant.

Magnesium may be prepared by the process employed for alu-

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minium, which, however, must be slightly modified, as magnesium is lighter than the scoria from which it is produced. 600 grms. of carefully prepared chloride of magnesium are mixed with 100 grms. of fused sea-salt (or better, of a mixture of chloride of sodium and potassium) and 100 grms. of pure fluoride of calcium, the whole previously powdered. 100 grms. of sodium in fragments are added and mixed intimately with the powdered chloride, and the whole is thrown, by means of a little iron spatula, into a red-hot earthen crucible, which is closed with its cover. In a short time the reaction takes place. When all noise has ceased, the crucible is uncovered, and the mixture is stirred with an iron rod until all the fused parts are homogeneous and the upper part of the bath is well exposed, when the globules of magnesium are distinctly seen. The crucible is allowed to cool away from the fire, and when the saline mass is ready to solidify, it is again stirred with the iron rod, and all the little metallic masses are collected so that they may form a single one; the whole is then poured upon a plate of iron. By breaking up the scoria the globules of magnesium may be removed, and the scoria may be fused once or even twice, affording a little more magnesium each time; 600 grms. of chloride of magnesium, with 100 grms. of sodium, gave 45 grms. of magnesium.

The crude magnesium is put into a charcoal tray, enclosed in a tube of charcoal, and heated nearly to whiteness, whilst a slow current of hydrogen traverses the apparatus. The tube is strongly inclined in the furnace, and all the magnesium condenses in front of the tray and is easily collected when the tube is cold. It is then fused in a mixture of chloride of magnesium, chloride of sodium, and fluoride of calcium. By gradually increasing the quantity of the latter, which is added by degrees to the fused bath, the scoria is rendered less fusible than the magnesium, so that the latter may be poured off just as the scoria is about to solidify.

When the current of hydrogen is strong in the distillation of magnesium, a small quantity of a fine metallic powder is carried a good way, and remains suspended in the hydrogen which escapes from the apparatus. If this gas be ignited it produces a most beautiful flame.—*Comptes Rendus*, Feb. 23, 1857, p. 394.

On the Preparation of Gallic Acid. By F. Steer.

The author's process is essentially a combination of the modes of preparation long since described by Scheele and Braconnot. 100 pounds of the best black Turkey galls are pounded as fine as possible, stirred up with water into a thin paste, and left standing for ten days, during which it is frequently stirred, and mixed with fresh water to replace that which is absorbed. Towards the end so much water is added that after it has quietly settled there may be 3 inches of it at the top; the supernatant fluid is decanted and preserved.

The paste which remains is put into a wooden vessel, adapted

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for extraction by displacement by water; everything soluble is then extracted.

The whole of the extracts are poured together, allowed to settle completely, decanted and strained into large stone-ware dishes, which are placed in winter in the neighbourhood of a warm chamber stove, but in summer in the open air, lightly covered. They are left standing until all the gallic acid has separated, for which purpose from three to four months are required. The mother-liquors are poured off, and the yellowish-red gallic acid, which crystallizes in transparent cubes, is washed several times with distilled water and dried. From the above quantity 24 pounds of gallic acid are usually obtained.

Before this acid is bleached, it must first of all be freed from the flocculent resinous matters, which would otherwise stop up the filter. The acid is dissolved in boiling distilled water, allowed to settle whilst warm, and decanted into another glask flask; pure animal charcoal is then added to it, it is again heated and filtered whilst hot through white filtering paper. The filtrate is heated afresh, poured into the crystallizing dish, which must previously be warmed and left to stand quietly and well covered for twenty-four hours.

The crystalline cake when taken out must be immediately wrapped up in white filtering paper, as otherwise the moist apices of the crystals are rendered black by ferruginous dust-particles floating in the air; subsequently the black colour diffuses itself to the bases of the crystals, which, however, produces a remarkably beautiful appearance.

Although gallic acid is but little employed at present, except in the preparation of pyrogallic acid for photography, it is nevertheless to be expected that it will one day find frequent employment in dyeing.—*Sitzungsber. der Akad. der Wiss. zu Wien*, xxii. p. 249.

On Bichromate of Copper. *By* F. Droege.

The existence of a crystallizable compound of oxide of copper with chromic acid has not yet been ascertained. H. Kopp, who experimented on the chromates, obtained green crystals by the treatment of hydrated oxide of copper with chromic acid; these, however, proved on analysis to be sulphate of copper, containing a small quantity of chromic acid. L. Gmelin also endeavoured in vain to prepare a crystallized salt.

At the recommendation of Professor Fresenius I made some experiments on this subject. To prepare the compound, I poured a concentrated solution of chromic acid over hydrated oxide of copper; the acid was prepared by Fritzsche's method, and once recrystallized. The hydrated oxide of copper dissolved readily; a brown fluid was produced, and an insoluble reddish-brown powder separated. From its external properties the latter appears to be ¼-chromate of copper. I filtered the solution through asbestos, and placed it in a flat dish, beside sulphuric acid under a bell-glass. After some time green crystals were formed, which were

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also obtained by Kopp, and after the removal of these, the fluid contained no more sulphuric acid.

By further evaporation over sulphuric acid, the solution became syrupous and covered with a crystalline film; I pierced this and poured the mother-liquor away. The crystalline film consisted entirely of very beautiful crystals of 2–3 millims. in length, and of a brownish-black colour; the bottom of the dish was covered with crystals, but a large quantity of the insoluble brown salt had been formed, and this was mixed with the crystals. After recrystallization I obtained the salt in a pure state; it dissolved completely in water.

The analysis was effected by first reducing the chromic acid by treatment with muriatic acid and alcohol, then precipitating the copper by sulphuretted hydrogen, and the oxide of chrome from the filtrate by ammonia. The analysis gave—

		Calculated.	Found.	
			I.	II.
CuO	39·68	24·9	25·34	25·02
$2CrO^3$	101·56	63·8	63·74	63·86
2HO	18·00	11·3	10·66	11·12

The direct determination of the water gave 11·95 and 11·99 per cent. The excess of water is caused by the great avidity with which the salt attracts moisture from the air.

Bichromate of copper forms brownish-black crystals, which dissolve very readily in water and deliquesce into a syrup in the air; in alcohol they also dissolve, and in ammonia with a green colour.

When the aqueous solution is boiled, a large quantity of the brown insoluble salt is produced; at 212° F. all the water is driven off; by ignition the compound is decomposed, oxygen is expelled, and oxides of copper and chrome are left.—Liebig's *Annalen*, January 1857, p. 39.

On the Preparation of Pyrogallic Acid. *By* Prof. Liebig.

The author has already called attention to the advantages of the employment of pyrogallic acid in photography; it has since almost entirely taken the place of gallic acid. He now gives a process for its preparation, which he regards as the most advantageous and which he has employed for the last three years.

The material required is crystallized gallic acid; when decomposed by heat, it furnishes the most beautiful pyrogallic acid in very large quantity. There is no saving in the employment of dried gall-nuts or their dry extract.

For this purpose the gallic acid is strongly dried, mixed with twice its weight of coarsely powdered pumice-stone, and exposed to its temperature of decomposition in a current of carbonic acid. The mixture of gallic acid and pumice-stone is put into a tubulated retort, of which it does not fill more than one-fourth; the retort is placed in a sand-bath, and surrounded with sand nearly up to its

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tubulure. A glass tube is inserted into the tubulure, through an india-rubber tube, and connected with an apparatus for the evolution of carbonic acid; the tube reaches deeply into the belly of the retort, so that its opening is about ¼ inch from the mixture.

The neck of the retort, which must be tolerably wide, reaches about 8 inches beyond the margin of the sand-bath, and is loosely inserted into a corresponding receiver, so that the latter may be easily removed. The object of this arrangement is easily understood. Dry gallic acid is decomposed at a high temperature into pyrogallic acid, metagallic or melanogallic acid, carbonic acid and water; the author has supposed that from 2 atoms of gallic acid, $C^{28} H^{12} O^{20}$, there are formed 2 atoms of pyrogallic acid and 1 atom of metagallic acid, $C^{12} H^4 O^4$, with elimination of 4 atoms of carbonic acid and 2 atoms of water, so that 100 parts of dry gallic acid should furnish 39 parts of pyrogallic acid. But as pyrogallic acid is decomposed into water and metagallic acid nearly at the same temperature at which gallic acid is decomposed, the procuring of 39 per cent. of pyrogallic acid depends essentially on the rapidity with which the acid is removed from the retort during its formation, and on the vapours being prevented from condensing in the upper part of the retort; for in this case it is impossible to avoid the fusion of the crystals and the flowing down of the fused pyrogallic acid into the belly of the retort in which it is decomposed. The current of carbonic acid serves to avoid this source of loss, but it also effects another object. In the current of gas the water formed retains its vaporous form at those places in the neck of the retort on which crystals of pyrogallic acid are deposited; in the receiver, where vapours of pyrogallic acid and water condense simultaneously, a syrupous aqueous solution is obtained instead of the crystals; from this, pyrogallic acid may be procured by evaporation, although never colourless.

It would be most advantageous to heat the gallic acid in a bath of *constant* temperature; this can never be attained by a sand-bath placed over a furnace, and the current of gas must therefore be regulated according to the temperature. Thus if drops of fused pyrogallic acid are deposited in the upper part of the retort, the heat must be increased and the current of gas slackened.

When the decomposition is going on, the wide neck of the retort becomes filled very rapidly with long, broad, flat, shining, white needles, which are removed with a feather. If the neck of the retort reaches the temperature of fusion of pyrogallic acid, it runs together, and solidifies lower down into a solid crust, which is removed with a silver spatula; during fusion the acid acquires a reddish colour, which persists after solidification and cannot be got rid of by charcoal. By this method, 31–32 per cent. of solid crystallized pyrogallic acid are obtained; the 8–9 per cent. which are lost according to the above calculation, give the carbonic acid evolved the appearance of a white smoke, and probably by a judicious arrangement of the apparatus some portion of it might be recovered.—Liebig's *Annalen*, January 1857, p. 47.

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On the Acids of Linseed-oil. *By* Dr. E. Schüler.

According to Sacc's investigations*, linseed-oil consists of the glycerine compounds of two acids, of which one is oily and fluid and the other solid and crystalline. Sacc found the melting-point of the latter to be 140° F.; he regarded it as margaric acid. The peculiar oleic acid to which linseed-oil is indebted for its ready oxidizability and resinification, was also analysed by Sacc, but he left it undecided whether its composition ought to be expressed by the formula HO, $C^{16} H^{38} O^5$, or by HO, $C^{46} H^{38} O^4$.

Of the composition of the peculiar acids in poppy-oil, nut-oil, hemp-oil, and other drying oils, with the exception of castor-oil, nothing is known at present, and remarkably little even of the acids of linseed-oil; the author thought, therefore, that new investigations of the acids of this series of fatty oils, and especially of linseed-oil, were very desirable.

The oil which was pressed on purpose for this investigation in the cold, had a pure yellow colour, and a spec. grav. of 0·9347 at 55°·4 F.; at zero it became thickish, and deposited a small quantity of the glycerine compound of the solid acid.

The saponification, which was commenced with weak solution of soda and completed with one of the greatest possible strength, took place with comparative ease.

The saponaceous mass produced was very gelatinous, of a light yellow colour, and a peculiar sickly odour. After it had been repeatedly treated with salt and freed as far as possible from the lye, the soap was dissolved in a large quantity of water and precipitated by an excess of chloride of calcium. The lime-soap was granular and could be easily washed; it was freed from water by pressure, and left for some time in a cylinder with æther poured over it. The lime-salt of the oleaginous acid was easily dissolved and separated by filtration from that of the solid acid. The filtrate was decomposed by muriatic acid in the cold; the ætherial solution of the fatty acids was drawn off from the inferior aqueous stratum, and the æther distilled off in a current of hydrogen at the lowest possible temperature.

The acid left was rather thickly fluid and of a dark yellow colour; it was therefore not suited for analysis. To purify it, the alcoholic solution was mixed with an excess of ammonia, and the baryta-salt was prepared by the addition of chloride of barium. After complete washing and pressing, it was extracted by æther, which took it up in abundance, and gradually deposited it again in small warts and grains †. After repeated recrystallization the salt appeared perfectly pure; in the dry state it formed a snow-white loose powder. The pure linoleate of baryta was finally mixed

* Liebig's Annalen, li. p. 213, 1844.

† The baryta-salt cannot be recrystallized from alcohol without considerable loss; with the least heat it forms a yellow resinous varnish, which presents comparatively few points of contact to the alcohol. The lime-salt behaves in the same way.

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with æther free from alcohol in a stoppered bottle, and decomposed by muriatic acid in the cold; the solution was drawn off, and the æther distilled from it in a current of hydrogen.

To remove every trace of adherent moisture, the linoleic acid was kept for a long time *in vacuo* over sulphuric acid and a mixture of lime and sulphate of iron. It then formed a slightly yellowish, very liquid oil of spec. grav. 0·9206 at 57° F.; it was very refractive, had a slight acid reaction, and tasted at first mild, but afterwards harsh in the throat, just like ricinoleic acid. It did not solidify at 0° F.; after standing for ten weeks in the air in an open platinum crucible, it had increased 2 per cent. in weight and become tenacious and thickly fluid; a thin stratum of it laid upon wood formed a varnish-like coat; upon glass the stratum became very tough in course of time, without forming a varnish. With nitrous acid it became thick and reddish, but deposited no crystals like elaidic acid. Analysis gave—

	Found.						
	I.	II.	III.	Average.		Calculated.	
C	76·10	75·89	76·23	76·07	32	192	76·19
H	11·40	11·12	10·93	11·15	28	28	11·11
O	12·50	12·99	12·84	12·78	4	32	12·70

Linoleic acid therefore is the first of a new series of fatty acids, in which the equiv. of carbon exceeds that of the hydrogen by 4, whilst in the ordinary oleic acids the difference is 2 equivs.

To confirm the formula, the author has analysed some of the salts, but could obtain no concordant results. The quantity of base found was always too small, from which he thought at first that linoleic acid must contain 2 equivs. of carbon and hydrogen, more than is given in the above formula. But as repeated combustions always gave concordant results, he concludes that the variation in the analysis of the salts must arise from the tendency of linoleic acid to form acid salts, like all the other fatty acids with a high atomic weight.

The author does not consider that there is any reason for regarding the solid acid of linseed-oil as margaric acid. From its melting-point it might just as well be palmitic acid, and Sacc's analyses do not agree sufficiently with the formula of either acid. Most probably the crystalline acid is palmitic acid; both the acids of linseed-oil would then contain equal equivs. of carbon and oxygen, and differ in composition only in the amount of hydrogen.

$C^{32} H^{32} O^4$	$C^{32} H^{28} O^4$
Palmitic acid.	Linoleic acid.

There would thus be a similar relation between these acids, as between benic acid, $C^{30} H^{30} O^4$, and moringic acid, $C^{30} H^{28} O^4$, which were found together by Walter * in the oil of the fruits of *Moringa aptera*.—Liebig's *Annalen*, February 1857, p. 252.

* Comptes Rendus, xxii. p. 1143 and Liebig's Annalen, lx. p. 271.

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On Acetal. *By* A. Wurtz.

Stas regarded acetal, $C^{12}H^{14}O^4$, as a compound of 1 molecule of aldehyde, with 2 molecules of æther. The following experiments prove that acetal really contains two groups of æthyle.

Acetal dissolves in concentrated muriatic acid. In a few days this solution becomes black, and then contains a considerable quantity of muriatic æther in solution.

Perchloride of phosphorus acts violently upon acetal, and evolves muriatic æther in abundance. If acetal be heated in sealed tubes with monohydrated acetic acid, 1 equiv. of acetic æther is obtained from 1 equiv. of acetal. Acetal may therefore be regarded as *glycoldiæthyline*, $\left.\begin{matrix}C^4H^4\\(C^4H^5)^2\end{matrix}\right\}O^4$, that is glycole, $\left.\begin{matrix}C^4H^4\\(H)^2\end{matrix}\right\}O^4$, in which the $(H)^2$ are replaced by 2 equivs. of æthyle. The author concludes that this opinion is correct, because it is possible to prepare mixed æthers in which various alcohol groups replace this H^2. Thus when acetal is prepared from a mixture of wood-spirit and alcohol, instead of from the latter alone, by distilling it with brown oxide of manganese and sulphuric acid the mixed alcohols

$$\left.\begin{matrix}C^4H^4\\(C^4H^5, C^2H^3)\end{matrix}\right\}O^4, \text{ and } \left.\begin{matrix}C^4H^4\\(C^2H^3)^2\end{matrix}\right\}O^4$$

are obtained.

The latter body was obtained when 300 parts of sulphuric acid and 200 parts of brown oxide of manganese were put into a retort with a mixture of 110 parts of alcohol and 90 parts of wood-spirit. As soon as the first swelling up was over, so much was distilled off as equalled the quantity of the two alcohols.

It is rectified by fractional distillation, and the portions passing at 149° and 185° F. are collected by themselves. Both portions are rectified and treated with chloride of calcium and caustic potash, and the fractional distillation is repeated in order to separate small quantities of methylal and acetal.

The body with a boiling-point of 149° F. in the pure state has the formula $C^8H^{10}O^4$, so that it is a mixed alcohol consisting of methylal and acetal:—

$$\text{either } \left.\begin{matrix}C^4H^4\\(C^2H^3)^2\end{matrix}\right\}O^4, \text{ or } \left.\begin{matrix}C^2H^2\\(C^4H^5, C^2H^3)\end{matrix}\right\}O^4;$$

it is a colourless, mobile fluid of an ætherial odour, resembling the other methyle compounds. Spec. grav. $=0{\cdot}8555$. It is soluble in a very large quantity of water, and burns with a white, luminous flame, edged with blue.

The other body with a boiling-point of 185° F., methylacetal, $C^{10}H^{12}O^4$, or $\left.\begin{matrix}C^4H^4\\(C^4H^5)(C^2H^3)\end{matrix}\right\}O^4$, is a mobile fluid of a penetrating odour, similar to that of acetal. Its spec. grav. $=0{\cdot}8535$. Density of vapour found 3·475, calculated 3·544. It is soluble in alcohol in all proportions, and in fifteen times its volume of water. Water, and especially an aqueous solution of chloride of calcium, precipitates the fluid. Caustic potash does not decompose this body.—*Annales de Chim. et de Phys.*, 3 sér. xlviii. p. 370.

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On the Compounds of Tantalum with Sulphur. By H. Rose.

Sulphuret of tantalum has been prepared in two methods; either by the decomposition of tantalic acid by sulphuret of carbon, or by that of perchloride of tantalum by sulphuretted hydrogen.

The conversion of tantalic acid into sulphuret of tantalum by the vapour of sulphuret of carbon, takes place as completely as possible only at a temperature near a white heat. The sulphuret thus obtained is greyish-black, but if it be triturated in a small agate mortar, it acquires a metallic lustre, and a very distinct brassy yellow colour. It is a good conductor of electricity.

If this sulphuret of tantalum be exposed to the action of chlorine gas, it is not attacked thereby at ordinary temperatures; when heated it is converted into perchloride of tantalum and chloride of sulphur, which may be volatilized, whilst a small quantity of a black woolly residue is left, which, even when strongly heated, resists the action of chlorine gas, and consists essentially of sulphuret of tantalum of great density. From the analysis by means of chlorine gas, as well as from the calcination of the sulphuret, by which it is converted into tantalic acid, it appeared that the sulphuret of tantalum has not the constitution of tantalic acid, but contains less sulphur. At the elevated temperature which must be employed in the preparation of sulphuret of tantalum, $2Ta+3S$ is probably formed; this, however, takes up some more sulphur during its gradual cooling in an atmosphere of sulphuret of carbon, but never so much as to produce the sulphuret corresponding to tantalic acid.

If this sulphuret be heated in a current of hydrogen it loses some sulphur, but still retains the property of exhibiting a brassy yellow colour when triturated in an agate mortar.

When tantalic acid has been converted into sulphuret of tantalum by sulphuret of carbon, and the metallic sulphuret is again oxidized to tantalic acid by ignition in the air, the quantity of tantalic acid employed is recovered exactly. This indeed might be expected, but it will be seen hereafter that the result of this experiment possesses a certain importance.

When tantalic acid is ignited in a glass bulb tube in an atmosphere of sulphuret of carbon, a sulphuret of tantalum of less density is obtained; this may still contain some tantalic acid. The density of the metallic sulphuret obtained also varies, according as the acid employed was prepared from the perchloride, or from tantalite by fusion with bisulphate of potash.

These kinds of sulphuret of tantalum, as well as that prepared at a white heat, acquire a brassy yellow colour when triturated in an agate mortar, but they are essentially distinguished from the latter by their losing more sulphur when ignited in a current of hydrogen, and then remaining black when triturated in the agate mortar. They also show a peculiarly different behaviour towards chlorine gas. They are attacked by this even at ordinary temperatures, and after the volatilization of the chloride of sulphur and perchloride of tantalum, leave quantities of tantalic acid which are often considerable.

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A pure sulphuret of tantalum of less density than that prepared from tantalic acid by means of sulphuret of carbon at a white heat, is obtained when perchloride of tantalum is decomposed by means of sulphuretted hydrogen. At the ordinary temperature the action is very slight; it takes place principally only when a mixture of vapours of the chloride and sulphuretted hydrogen is strongly ignited; when the heat is less the chloride may be volatilized in the sulphuretted hydrogen gas, without being much decomposed. In this case no traces of water are formed, a proof that perchloride of tantalum, when well prepared, contains no oxychloride.

The sulphuret obtained in this way is of a pure black colour, but when triturated in an agate mortar it exhibits a metallic lustre, and a brassy yellow colour; sometimes also it is obtained in the form of crystalline crusts of a brassy yellow colour, not unlike iron pyrites. It is a good conductor of electricity. It is very strongly attacked by gaseous chlorine even at ordinary temperatures; and after the perchloride of tantalum and chloride of sulphur have been driven off, it leaves but a small quantity of a white residue of tantalic acid, which can only be produced by the violent action of the chlorine upon the sulphuret, whilst the latter was still surrounded by atmospheric air.

On examination it appeared that this sulphuret consisted essentially of $2Ta+3S$, with only a somewhat smaller quantity of sulphur.

If sulphuretted hydrogen gas be passed over tantalic acid during ignition, only a very small quantity of sulphuret is formed. The acid is rendered gray. When the vapours of sulphuret of carbon are conducted over heated perchloride of tantalum, no decomposition takes place.—*Bericht der Akad. der Wiss. zu Berlin*, 1856, p. 599.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On Soluble Glass, its Preparation and Applications. *By* J. N. von Fuchs.

In the introduction to this memoir the author refers to the length of time that his discovery, which was made in 1825, remained unnoticed, being at first declared of no consequence, and even attacked. Before his departure from the world, as the celebrated author says, he feels himself impelled, now that the importance of this discovery has been recognized, to publish another series of observations in this memoir. In the first section the author describes the mode of preparation of the four different kinds of soluble glass, the nature and employment of which were treated of by him in his previous papers. These are:—

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1. *Soluble Potash Glass.*—This is prepared with—

15 parts of powdered quartz or pure quartz-sand,
10 ... well-purified potashes,
1 ... powdered charcoal.

On a large scale we may take

45 pounds of quartz,
30 ... potashes,
3 ... charcoal powder.

These ingredients are well mixed and fused for five or six hours in a fire-proof glass crucible with a strong fire until the whole has reached a uniform and quiet fluid state, for which purpose no lower temperature is required than that for the fusion of ordinary glass. The fused mass is then taken out with iron ladles, and the crucible again filled with a new charge.

The glass thus obtained is pulverized, and gradually put into about five parts of boiling water in an iron kettle; it is constantly stirred, and fresh hot water is frequently added to replace that which evaporates, and the whole is kept uninterruptedly boiling until it is dissolved, with the exception of a muddy deposit, and a tough film capable of being drawn out into threads is formed upon the surface (this takes from three to four hours). This film indicates that the solution is approaching concentration; it disappears again, however, when it is immersed, after which the boiling is continued for a short time in order to bring the solution to the proper state of concentration, in which it has a specific gravity of 1·24 to 1·25. At this strength it is still tolerably fluid, and capable of being employed at once in many cases; for certain purposes, however, it must be diluted with more or less water. It may also be evaporated further until it reaches the consistence of a syrup, but it can then only be employed with advantage in particular cases.

When, as is not unfrequently the case, it contains some sulphuret of potassium, some oxide of copper or copper scale is added towards the end of the boiling in order to destroy it; by this means a small portion of potash is set free; but this is not only not injurious for most technical purposes, but is even advantageous in many. But if it be desired to have a soluble glass completely saturated with silica, it must be boiled with freshly-precipitated silica until no more of this is dissolved.

To facilitate its transport, it may be evaporated with constant stirring until it forms a soft mass; and the best vessels for packing it are made of tinned iron. A better and more ready means of preparing it in the solid state is furnished by alcohol. Thus if the concentrated solution be mixed with one-quarter volume of rectified alcohol, a gelatinous precipitate is produced; this in the course of a day or two contracts strongly, and adheres firmly to the bottom of the vessel. If the supernatant fluid, which not unfrequently contains besides some carbonate of potash, traces of chlorides of potassium and sodium and sulphuret of potassium, be poured away, and the precipitate washed with water and slightly pressed, the soluble

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glass is obtained in a solid state, very pure, and completely saturated with silica. It is readily and perfectly soluble in water. When the expression soluble glass alone is used in the following pages, the potash glass is always to be understood.

2. *Soluble Soda Glass* is prepared from

45 pounds of quartz,
23 ... anhydrous carbonate of soda,
3 ... charcoal powder.

This mixture is somewhat more readily fusible than the potash-glass. It may be most cheaply prepared, however, as Professor Buchner has ascertained, by means of Glauber's salts, for which purpose take

100 parts of quartz,
60 ... anhydrous sulphate of soda,
15–20 ... charcoal.

The product, when completely saturated with silica, furnishes with water a somewhat more opalescent solution than that prepared with potash at the same degree of concentration.

It is not precipitated completely at once by rectified alcohol, like the potash-glass, but only converted into a gelatinous mass; when it is not completely saturated with silica and somewhat diluted, it either gives no precipitate or only furnishes one after some time, by which it may be easily recognized and distinguished from the potash-glass.

3. *Double Soluble Glass.*—Potash- and soda-glass may be mixed together in all proportions, but we can only regard as a normal double glass that which contains equal equivalents of potash and soda, and which may be obtained with certainty with Rochelle salt and the requisite quantity of quartz (100 parts of quartz to 121 parts of Rochelle salt). But this is too expensive for technical purposes, and it may be prepared much more cheaply with equal equivalents of nitrates of potash and soda, or purified tartrate of potash and nitrate of soda, and the corresponding quantity of quartz; this is of sufficiently good quality for technical purposes. It may also be prepared by the direct fusion of quartz, carbonate of potash, and carbonate of soda, according to the following recipe:—

100 parts of quartz,
28 ... purified potashes,
22 ... neutral anhydrous carbonate of soda,
6 ... charcoal powder.

It fuses perceptibly with greater ease than either of the preceding.

As it is of no consequence for technical purposes to have an exact quantitative proportion, it will not be far wrong to mix 2 parts by measure of concentrated soda-glass with 3 parts by measure of potash-glass; this will give a double glass which is applicable to all technical purposes, for which it is found to be particularly adapted.

4. *Soluble Glass for Fixing.*—The ordinary soluble glass is not adapted to stereochromic purposes; the figures which are fixed by

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it acquire spots. Soluble glass for this purpose is prepared by fusing together 3 parts of pure anhydrous carbonate of soda with 2 parts of powdered quartz. Of this a concentrated solution is made in water, and 1 part by measure of this is mixed with 4 to 5 parts by measure of concentrated potash-glass completely saturated with silica, by which means, besides an increase of silica, it acquires a larger amount of alkali which is sufficient to prevent its rapid decomposition without perceptibly altering its other properties. The soluble glass which was previously turbid or opalescent, becomes perfectly limpid and rather more fluid by this means. The use of this mixture is not limited to stereochromy, but it may also be applied with advantage to many other purposes.

Properties of Soluble Glass, and its behaviour to other Bodies.—The solid, or fused soluble glass, which, when pure, has the appearance of ordinary glass, dissolves gradually in boiling water, without leaving a residue; in cold water, however, the solution takes place so slowly, that it might almost be supposed to be quite insoluble therein. It is, however, quite insoluble only when a much larger quantity of silica is combined with it, or a part of its potash is extracted from it, or when other bodies, such as earths, metallic oxides, &c., are present in it, which combine with it to form triple or double salt-like compounds, such as we meet with frequently in the mineral kingdom: common glass is also a compound of this nature. It must be observed, in passing, that silica generally combines rather with two bases than with only one.

Acids, even including carbonic acid, decompose the solution, and separate the silica in the gelatinous form. They act still more strongly and rapidly, even when diluted, upon the solid soluble glass, and separate the silica from it in the pulverulent form.

Salts with alkaline bases, especially carbonates and muriates, produce pasty precipitates, which are formed immediately, and coagulate the whole fluid when it is not too much diluted; otherwise they only make their appearance slowly. In this respect muriate of ammonia is peculiarly active, and produces a flocculent precipitate, with evolution of ammonia, even when the solution is greatly diluted: this precipitate, when washed for a long time with water acidulated with nitric acid, leaves pure silica.

The alkaline earths set free more or less potash from the solution, and combine with the silica and the rest of the potash to form double compounds, which are completely insoluble in water.

Alumina also combines with it to form a product insoluble in water, for which reason it is necessary to see that the quartz-sand which is employed in the preparation of the soluble glass bears no argillaceous particles with it. The insoluble paste produced in the solution of the fused glass probably arises principally from the alumina taken up by the glass from the melting-pot. If soluble glass be exposed to the air in solution in open vessels, it attracts carbonic acid, and undergoes decomposition, so that it coagulates in a longer or shorter time, and a gelatinous deposit gradually forms, which, according to Buchner's investigation, contains potash.

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With the aid of heat, this change takes place much more rapidly than at the ordinary temperature; and if the solution be gradually evaporated in a dish on the evaporating furnace, and at last exposed to a stronger heat, in order to render it anhydrous, during which operation it becomes strongly inflated into a pumice-like mass, it is found afterwards to be for the most part decomposed, rendered insoluble in water, and capable of effervescing strongly with acids. By a slight red heat, however, it again returns to its original state, so that it may be completely dissolved in water.

From this it appears that when it is desired to prepare soluble glass in the solid state from its solution by evaporation, it must be kept constantly boiling, when the access of the carbonic acid is prevented by the steam. The same thing has to be taken into consideration in the solution of the crude fused glass; for which reason cold water must not be employed to replace that which is evaporated, because otherwise the boiling would be interrupted, and the access of carbonic acid would be permitted.

When solid, pulverized, soluble glass is exposed for some time to the air, it undergoes the same alterations as during evaporation; thus it effervesces strongly with acids, and only dissolves partially in water, leaving a strong sediment. But if the powder be calcined, it again dissolves completely. If drops of it be let fall upon the table or the floor, they soon lose their transparency, and become white, in consequence of partial decomposition. The same thing takes place when it is poured out of a glass vessel, in which case some of it frequently runs down on the outside, and remains adherent; it then soon after drying, forms white streaks, which cannot easily be got rid of. If it be preserved in a glass vessel which is not quite full or well stopped, a white ring is produced in course of time, and this adheres so firmly that it cannot be entirely got rid of, even with acids. At the same time a more or less considerable precipitate is formed at the bottom of the vessel.

If concentrated soluble glass be laid upon a solid material which imbibes it very little or not at all, such as glass, marble, thick paper, &c., it soon dries and forms a shining transparent varnish, which, however, does not long remain in this state, but gradually becomes dull, turbid, and sometimes cracked, and at last acquires a delicate dusty coating. This alteration is due to the fact that air-dried soluble glass still contains much water (about 12 per cent.), which it only loses slowly; and during this it always contracts more and more, and acquires considerable hardness.

One of the most excellent and important properties for technical purposes possessed by soluble glass is that of binding and rendering coherent; it serves therefore to give loose masses density and a stronger cohesion, to unite separate parts of bodies, to combine small fragments into a larger whole, to fill up clefts and cracks, &c., in which direction it has by no means attained all the applications of which it is capable. In this respect it may be compared with glue, and it might be called mineral glue.

Its efficacy is shown immediately when it is incorporated with

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solid and porous bodies which imbibe it, and when it is brought in contact with pulverulent, dusty, or sandy bodies, or such as may be crushed between the fingers; by this means these are converted into stony masses, and at the same time the glass loses its solubility in water.

These actions are dependent as to their degree upon the nature of the substances with which the soluble glass is brought in contact, as some attract and unite with it more strongly than others. In this respect the essential difference occurs, that with some, such as magnesia and oxide of zinc, a chemical combination takes place with the glass, whilst in other cases the only action is that of the adhesive power.

In the former the actions, namely hardening and insolubility, are easily intelligible, as an insoluble product is formed by the reception of a second base; in the latter it is not so easy to understand the process, especially as the behaviour of the soluble glass to bodies of different kinds differs considerably; for which reason also it is by no means a matter of indifference what body is selected when it is desired to prepare an intimate, solid, water-proof mixture. Thus, soluble glass gives a much greater adhesive tendency to powdered marble than to powdered quartz. That the carbonic acid of the air assists greatly in the consolidation of soluble glass is evident even from what has already been said regarding its partial decomposition by the action of the air: this, however, does not appear sufficient to explain the remarkable change which is often perceptible even in a few days. Carbonic acid certainly loosens the otherwise weak union between the silica and alkali; but, in the author's opinion, the silica does not behave passively, but, in accordance with its very peculiar nature, spontaneously acquires various states of coherence, and even assists actively, itself contracting, so to speak, and at the same time uniting so firmly with the bodies in contact with it, towards which it has a coherent tendency, that the whole becomes, as it were, petrified. With a mixture which does not bind in the desired manner, it is only necessary to add some material which enters into a chemical combination with the soluble glass, when the desired result is certain to be attained.

A good binding mixture of pulverulent or sandy materials with soluble glass, is called *soluble-glass mortar* by the author. In many cases, as we shall see hereafter, it may be employed with great advantage instead of the ordinary lime-mortar.

To the porous bodies by which soluble glass is imbibed it communicates an extraordinary solidity. In this category are included almost all objects of burnt clay, such as bricks, tiles, furnace-tiles, pottery, &c., as well as loose limestones and sandstones, and woodwork.

The material which is especially applicable to technical purposes in combination with soluble glass is—

a. Carbonate of lime (chalk, calcareous sand, powdered marble).—When powdered chalk is made into a paste with water, well dried, and soaked with soluble glass, it furnishes a very compact mass,

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According to Buchner, if a fragment of chalk be immersed in moderately concentrated soluble glass, and left in it for about two days, then taken out, dried, and again laid in a more dilute soluble glass for a time, it is completely penetrated by the glass, and when dried, acquires a hardness throughout which approaches very closely to that of marble: it receives a good polish, and does not soften in the least in water, which only acquires a weak alkaline reaction from it. It has also acquired a considerable density. Von Liebig and Buchner have very recently convinced themselves of this remarkable behaviour of soluble glass by their own experiments. Chalk consequently furnishes an excellent addition to soluble glass, to bind it firmly and render it insoluble in water.

b. Dolomite appears, from experiments very recently made with it, to excel even limestone in its binding power; and as it is distinctly harder than limestone, the mass prepared with its powder acquires even by this means a greater power of resistance to external actions, both mechanical and chemical. At any rate, it is one of the best means of binding soluble glass, and rendering it insoluble in water; and as it occurs very abundantly in nature, and is widely diffused, it may be obtained almost everywhere without any great expense.

c. Phosphate of Lime (Bone-earth).—Phosphate of lime also furnishes a very compact mass with soluble glass; this hardly differs from that formed with carbonate of lime, although no chemical action or conversion of the constituents takes place.

d. Caustic lime.—When triturated with slaked lime, soluble glass quickly stiffens, and then dries slowly into a tolerably hard mass. In this case a chemical combination of the lime with the glass takes place, and potash is separated, when a sufficient quantity of soluble glass is present. Of course, water cannot injure this product. It may often be employed with good results as an addition to other masses which do not combine well; the addition, however, must be small, as otherwise the penetration of the soluble glass is prevented.

e. Lime disintegrated by exposure to the air (semicarbonate of lime).—This acts very well with soluble glass when triturated therewith; it does not stiffen (coagulate), and dries gradually into a solid mass, which is a chemical product consisting of silicates of potash and lime. This may be very serviceable as an addition to other masses; and as caustic lime is soon converted into semicarbonate by the action of carbonic acid in the air, walls built with lime-mortar may be, after some time, soaked with soluble glass, in order to give them greater solidity.

f. Powdered Quartz.—Powdered quartz, however fine it may be, exhibits no great adhesiveness with soluble glass, which could hardly have been supposed. If a mortar-like mass be made with it, and this be spread upon a tile previously soaked with soluble glass, it dries in a few days into a solid mass, which resists rain, and acquires a stony hardness on the surface. But when this surface is broken through, the interior is found to be quite soft and destitute of soluble glass, which has concentrated itself at the surface. It can only

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receive a perfectly uniform consistence by frequent soaking with soluble glass.

The case is very different when the powder is first mixed with a little lime disintegrated in the air, then treated with soluble glass, and twice subsequently impregnated therewith. In this way the mixture becomes so compact as to leave scarcely anything to be desired.

The same thing takes place with lime-mortar to which quartz-sand has been added, when it is treated with soluble glass after it is thoroughly dry.

g. Burnt Clay and Porcelain Earth.—These bodies also are amongst those with which soluble glass does not combine strongly. Here also the soluble glass collects towards the surface, and leaves a loose powder in the interior, which can only be bound together by frequent additions of soluble glass.

Objects made of different kinds of clay behave very differently when they have been burnt, and, as is usually the case, are porous, so that they imbibe the soluble glass. For example, if a burnt plate of potter's clay, which possesses no great solidity, and may easily be broken, be repeatedly drenched with moderately concentrated soluble glass, and dried after each soaking, it acquires such solidity as to be capable of opposing an obstinate resistance to both chemical and mechanical forces. A plate thus prepared, made out of the so-called sagger clay, not much more than half an inch thick, and so soft that it fell to pieces at the least pressure before its impregnation with soluble glass, is employed by Professor Kaiser as a covering-plate in his evaporating furnace, in which vapours of various kinds pass over it; but these have been as yet unable to injure it in a space of about twelve years. Not only plates, but articles of pottery of almost all kinds may be rendered solid and durable by soluble glass, that is to say, if they imbibe it well.

h. Oxide of Zinc (Zinc-white) *and Magnesia.*—These two bodies act very energetically upon soluble glass, and here also they exhibit their analogy, which may be recognized in many other chemical combinations, both natural and artificial.

Oxide of zinc may be triturated with soluble glass without the occurrence of any stiffening. This mass, when laid rather thick upon a solid support previously soaked with soluble glass, binds together slowly, and gradually hardens, during which it acquires a great many cracks, and breaks up into numerous small hard fragments, which separate from the support; these are not diffusible in water, to which they only give a slight alkaline reaction, whilst they retain their hardness. From this we may conclude that oxide of zinc enters into an intimate chemical combination with soluble glass.

If the mixture of oxide of zinc and soluble glass be only laid thinly upon the support, it remains firmly attached to it, and furnishes a good coating, to which any colour may be given at pleasure.

As this oxide possesses such a strong binding power, and its product with soluble glass presents such a complete resistance to the action of water, it is necessary to add a small quantity to those masses which do not bind sufficiently, mixing it intimately with

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them before the soluble glass is added. Even with masses which bind well a small addition of oxide of zinc is not only not injurious, but advantageous, by increasing their solidity, and, at all events, preventing the passage of the soluble glass to the surface.

Pure Magnesia, when triturated into a pasty mass with concentrated soluble glass, binds together more quickly than oxide of zinc, and hardens very greatly in drying; but when laid upon a solid basis to a greater thickness than card-board, it frequently cracks, and becomes for the most part loosened from its support. The fragments cracked off show considerable hardness when triturated. The water employed for this purpose has an alkaline reaction, but gives no turbidity with muriate of ammonia, proving that only a little potash is dissolved, but no silica, or at the utmost only a trace.

There is consequently no doubt that magnesia, like oxide of zinc, combines chemically with soluble glass, and like this, may be employed advantageously as an addition to other less binding masses.

With regard to the behaviour of carbonate of magnesia towards soluble glass, experiments have only been made with that kind which is known under the name of *Magnesia alba*; these all gave satisfactory results. The mass, made into a paste with concentrated soluble glass, and spread upon a glass plate, soon adhered, and in a few days acquired such solidity, that it held so firmly to the glass plate as to be only separated from it with difficulty with a knife. A few fragments of it were put into water, and digested for some time, when, although the consistence of the mass was not perceptibly altered, some carbonate of potash without silica was dissolved; muriate of ammonia produced no turbidity. A portion of it was pulverized and extracted with water in which some carbonate of potash was dissolved. A portion was mixed with dilute sulphuric acid, when a slight effervescence was gradually produced, magnesia was dissolved together with the potash still present, and silica was left behind in the form of powder, which dissolved easily and completely in solution of potash.

Magnesia alba and soluble glass consequently act chemically upon one another, the silica with a portion of the potash combining with the magnesia, at the same time that some carbonate of potash is formed. *Magnesia alba* consequently is one of the most excellent fixing agents for soluble glass.

i. Gypsum (hydrated sulphate of lime).—Gypsum, when triturated with soluble glass, sets immediately, and during desiccation a large quantity of sulphate of potash or soda effloresces very soon, according as potash- or soda-glass is made use of in the experiment. After drying, the mass is scarcely perceptibly firmer than ordinary plaster of Paris. A mutual chemical action takes place here unmistakeably. From this behaviour it appears that objects made of plaster of Paris cannot be impregnated with soluble glass to render them more solid and stable in the air, as in consequence of the quick setting it cannot penetrate into them. As a matter of course this body cannot be employed for the purpose under consideration; and in any operation undertaken with soluble glass and bodies to be mixed

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therewith, the formation of gypsum must be prevented, and still more must its presence ready formed in them be avoided.

Anhydrite (anhydrous sulphate of lime) and strongly calcined plaster which, according to the author's opinion, approaches this very closely, promise a better result; but nothing can be stated decidedly upon this point, as the experiments commenced therewith are not yet completed. These and many other experiments with various bodies as to their behaviour with soluble glass will be communicated hereafter. These bodies are, heavy spar, fluor-spar, oxide of iron, basic iron salts, litharge, white-lead, &c. The bodies here referred to, with their behaviour towards soluble glass, are sufficient for the present purpose.

In these experiments, as also in practice, the degree of concentration of the soluble glass employed is by no means indifferent: 1 part by measure of concentrated soluble glass to 2 parts by measure of water, should be the maximum, and 1 part by measure of the same glass to ½ part by measure of water the minimum of dilution, or sometimes a little less, according to circumstances.

If it be too much concentrated or diluted, it very often does not produce the effects required of it. If it be very concentrated, it does not penetrate easily or deeply enough into bodies which are to be impregnated with it; and if it be much diluted and made into a pasty mass with powdered bodies, these may appear sufficiently coherent at first when dried, but in a few days they are found to be more or less loose and soft, and the desired degree of solidity can only be obtained by frequent treatment with soluble glass. By the dilute soluble glass the particles of the body are kept too far apart, so that when the soluble glass has contracted, innumerable small interstices are produced, which interrupt the cohesion. The question arises also, as to how far the saturation of such bodies with soluble glass is to be carried, whether until they can take up no more soluble glass, and are completely closed, or only so far that they may remain to a certain extent permeable to it. In the former case the greatest possible solidity is attained; in the latter we gain the advantage of being able subsequently to apply colours, and fix them with soluble glass. The proper proportion must remain to be ascertained by those who set about the attainment of a particular object. It only remains to be remarked, that when a body is completely saturated with soluble glass and closed by it, it may be again opened to a certain extent when it is heated, or when alcohol is burnt upon it once or twice.

In course of time the pores open somewhat of themselves, especially when they are frequently exposed to rain, by which some alkali is carried off, and the silica gradually acquires the predominance, so that at last a complete petrification is effected, and the final object of this process is attained.

Potash-glass, which hardens when intermixed with pulverulent bodies somewhat more rapidly than the soda-glass, may perhaps also give them a rather greater solidity; but the difference is by no means considerable. The soda-glass, however, at any rate possesses

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an advantage over the former in its greater fluidity, in consequence of which it penetrates into the smallest interstices, pores and cracks with much more facility than the somewhat sticky and tough potash-glass. This is of some importance to masons and statuaries. As soda does not combine with silica so strongly as potash, and has a great tendency to effloresce by combining with carbonic acid, this might perhaps give an advantage to the soda-glass, because by this means the silica is more readily set free, and the silicatization of the mass is sooner attained; this, however, must be left to further observations.

The double soluble glass seems to unite the properties of the two preceding, and may perhaps deserve a general preference over them, because it contains two bases (potash and soda) with which silica, which prefers entering into double combinations, combines more powerfully.

The soluble glass for fixing, as already stated, has its own proper purpose, but it is also applicable to many other objects, especially in painting.

The first three kinds of soluble glass, when completely saturated with silica, are always more or less turbid or opalescent; this is attributable to imperfectly dissolved and extremely finely divided silica.

To deprive them of this, which may even frequently be economical, we need only add a little silicate of soda, and let them stand for about a day, with frequent stirring. By this means the turbidity completely disappears, the fluid becomes perfectly limpid, if it be not coloured by some other (organic) substance.

[To be continued.]

Manufacture of Sulphuric Acid from Gypsum. By Otto Köhsel.

This method, which is patented for the kingdom of Hanover, consists in the following processes:—

1. Calcination of a mixture of finely-ground gypsum and coal-dust in cylinders, by which carbonic acid gas is evolved and sulphuret of calcium is left.

2. The conducting of the carbonic acid evolved through a series of air-tight boilers, heated by the calcining furnace, and containing the sulphuret of calcium obtained in previous operations with a sufficient quantity of water; in these there is a formation of carbonate of lime, which is precipitated, and of sulphuretted hydrogen, which is evolved.

3. Immediate combustion of the sulphuretted hydrogen gas, and introduction of the sulphurous acid gas thus produced into the lead-chambers of a sulphuric acid factory. The further process does not differ from the ordinary one.—*Mittheil. des Gewerbever. für das Königr. Hannover*, 1856, p. 135.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

Researches on the Ammonia-cobalt Bases.
By WOLCOTT GIBBS *and* F. A. GENTH.

THE facility with which alkaline solutions of many metallic protoxides absorb oxygen from the air, attracted the attention of chemists at an early period. The protosalts of iron, manganese, and cobalt are particularly remarkable in this respect. In the presence of an excess of the fixed caustic alkalies and their carbonates, salts of the protoxides of these metals are more or less rapidly converted into basic salts of their higher oxides. A similar effect appears to be produced by all of the more powerful fixed bases, while it is remarkable that neutral or acid solutions of the same salts are oxidized much more slowly, an effect which is perhaps owing to the tendency which persalts in general exhibit to become basic, and to the influence which an excess of acid exerts in producing neutral or acid compounds.

Ammonia acts like potash and soda in causing the oxidation of solutions of iron and manganese. In the case of these two metals, either basic salts or hydrates of the peroxides are formed, which contain no ammonia, at least in chemical combination. With salts of protoxide of cobalt the result of the oxidation is very different. The sesquioxide of cobalt, at the instant of its formation, unites with a certain number of equivalents of ammonia, so as to produce a conjugate base of which ammonia forms an integral portion. The new base partakes in some measure of the properties of the alkalies, the peculiar character of the salts of cobalt being wanting. It is with this class of bases that we have at present to deal.

The earliest observations which we possess upon the oxidation of the salts of cobalt are due to Leopold Gmelin, who, in a memoir published in 1822*, described the changes of colour which are produced when ammoniacal solutions of the chloride, sulphate, and nitrate of cobalt are exposed to the air. The solutions under these circumstances absorbed oxygen and became brown, and Gmelin considered it probable that they contained a cobaltic acid. Dingler†, who subsequently endeavoured to determine the amount of oxygen

* Neues Journ. der Chem. und Phys., neue Reihe, v. 235.
† Kastner's Archiv, xviii. 249.

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absorbed, inferred that the cobaltic acid consisted of 1 equiv. of cobalt and 2 equivs. of oxygen, since the brown solution gave with sulphide of ammonium a black precipitate of bisulphide of cobalt. Winkelbleech* denied the existence of a metallic acid in the solution; but though his memoir contained many interesting and valuable contributions to our knowledge of the oxides of cobalt, it threw no light upon the true nature of the ammoniacal compounds, except by establishing in them the existence of sesquioxide of cobalt. The subject was next investigated by Beetz†, who analysed an ammoniacal sulphate and nitrate of sesquioxide of cobalt formed during the direct oxidation of ammoniacal solutions. These analyses led to the formulas $Co^2O^3, 3SO^2+3NH^3+NH^4O$, and $Co^2O^3, 3NO^5+3NH^3+NH^4O$; but as the substances employed were not crystallized, and as the analytical methods were difficult to execute, but little reliance could be placed in the results. Beetz, however, considered the sesquioxide of cobalt in these compounds as playing the part of an acid, the ammonia being present as a salt of ammonium.

The oxidation of ammoniacal solutions of various salts of cobalt was also observed by Rammelsberg‡, and the products of the action in several cases analysed. None of the formulæ obtained, however, appear to belong to well-defined and distinct compounds.

A memoir published by one of ourselves, in 1851§, contained the first distinct recognition of the existence of perfectly well-defined and crystallized salts of ammonia-cobalt bases; in fact, we have not been able to trace in any earlier paper even the idea of the existence of such a class of compounds. The results made public in this paper had been obtained by the author in Marburg in 1847, had been at that time freely though verbally communicated, and a suite of the salts obtained had been left in the laboratory at Giessen. Want of opportunity prevented a complete and systematic investigation, particularly from the analytical point of view. The memoir in question contained, however, besides several analyses, an accurate description of the two bases now to be described under the names of Roseocobalt and Luteocobalt. Though the analyses were from necessity not sufficiently complete and extended to fix the constitution of the bases in question, yet the fact is indisputable that this memoir contained, not merely the first announcement of the existence of ammonia-cobalt bases, but also a scarcely less accurate and complete description of two of these bases than any which has since appeared.

As its title states, the memoir in question was intended simply as a preliminary notice; circumstances, however, prevented a resumption and continuation of the subject. In a paper published in 1851||, Claudet described with some detail the properties of the chloride of purpureocobalt, and the mode of obtaining it, as well as a few other ammonia-cobalt salts. With the exception, however, of more complete analyses, the memoir in question contained nothing which is

* Ann. der Pharm., xiii. 148, 253.
† Pogg. Ann., lxi. 480, 490, 494.
‡ Pogg. Ann., xliv. 268; xlviii. 208.
§ Chem. Gaz., vol. ix. p. 286.
|| Phil. Mag., ii. 253.

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not to be found in the previously published paper above alluded to. In two notices communicated to the Academy of Sciences* in the same year, Fremy announced as his own the discovery of a class of compounds containing cobalt and ammonia, and produced by the oxidation of ammoniacal solutions of protosalts of cobalt. In the following year his complete memoir appeared†. In this Fremy describes anew the ammonia-salts of protoxide of cobalt, first obtained by H. Rose, then passes to the description of two new classes of compounds discovered by himself, and named by him oxycobialtique and fuscocobialtique, and finally describes at some length the principal salts of Genth's two bases, the constitution of which he correctly determines. Fremy appears not to have been aware that these two bases had been described in a manner little less complete than his own two years before the appearance of his memoir. The chloride of luteocobalt and its platinum-salt have also been described and analysed by Rogojski‡, and what we now term the chloride of purpureocobalt, by Gregory§, who corrected the analyses of Fremy.

The researches of Claus‖ on the ammonia-iridium and ammonia-rhodium bases established the existence of compounds of these metals exactly analogous to roseocobalt and its salts, and chemists will look with impatience for the publication of his results in detail. Recently Weltzien has published some theoretical views on the constitution of the ammonia-cobalt bases, which possess much interest.

The salts of xanthocobalt were discovered in November, 1852, by W. G.; and the principal results which are contained in the present memoir were communicated to the American Association for the Advancement of Science, at its meeting in Cleveland in August, 1853. The formulæ of several of the more remarkable bases are also given in a Report on the recent progress of organic chemistry, read before the same Association at its Providence meeting in August, 1855. The nomenclature of the ammonia-cobalt bases proposed by Fremy is so simple and convenient, that we have adopted and extended it to meet every case. We have, however, considered it desirable to drop the terminal syllable "iaque," employed by Fremy, not merely because it is not an English termination, but because by omitting it we obtain shorter and more convenient words. Thus we say roseocobalt and luteocobalt, instead of roseo-cobaltiaque and luteo-cobaltique, or roseo-cobaltia and luteo-cobaltia, which are the English equivalents. The shorter names, as will hereafter appear, also agree better with our own theoretical views, since we consider the compounds in question conjugate metals, and not ammonias.

With the view of making the description of our salts as complete as possible, we have followed the excellent example of Fremy, and referred the colours of these substances to Chevreul's chromatic scale. Fremy had the advantage of Chevreul's own determinations. We have employed for the purpose the chromatic scales recently published in Paris by Digeon, and which appear to be reliable; in

* Chem. Gaz., xi. p. 201.
† Ann. de Chim. et de Phys., xxxv. 257.
‡ Chem. Gaz. x. p. 95.
§ Ann. der Chem. und Pharm., lxxxvii. 125.
‖ Chem. Gaz. xii. p. 441.

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any event they give *some* precision to determinations of colour. As we have found that very many of the salts of the ammonia-cobalt bases exhibit a well-marked dichroism, we have in most cases examined the light reflected from layers of crystal by Haidinger's dichroscopic lens, and have given the colours of the ordinary and extraordinary images as obtained in this way. As a curious physical result, we may here mention that in general the cobalt colour predominates in the ordinary image.

We are indebted to Prof. Dana for the determination of the systems to which many of our crystals belong, and of their principal forms.

Methods of Analysis.

The accurate quantitative determination of the different elements which enter into the constitution of the ammonia-cobalt bases and their salts is attended with great difficulties. We have in general found it necessary to study out with much labour the methods of analysis proper to be used in each particular case; and it has been only after many trials that we have at length been able to obtain accurate results. Before proceeding to the description of the compounds in question, it may therefore be proper to state the analytical methods employed.

Cobalt.—The determination of the cobalt in these salts may, in most cases, be very easily and accurately effected by the following process. A weighed portion of the salt is gently heated, in a deep platinum crucible, with a quantity of pure and strong sulphuric acid sufficient to moisten the whole mass. Some effervescence is generally produced by the addition of the acid, but there is no danger of loss if the crucible be sufficiently large, and if the heat be applied only after the first action of the acid is over. The mixture is to be gently heated over a spirit-lamp until the excess of the acid, sulphate of ammonia, and other volatile matters have been expelled. During the whole time of heating, the cover of the crucible must be so placed as to prevent the possibility of loss by spattering, and at the same time to permit the escape of volatile matters. When, however, the quantity of acid has not been too great, the whole process goes on very quietly to the end, when the mass becomes dry. The heat is finally to be raised for an instant to low redness, the cover of the crucible being quickly lifted off and then replaced. The crucible is then to be allowed to cool, and weighed, when the quantity of cobalt may easily be calculated from the weight of the dry and pure sulphate. After the weighing, the mass in the crucible must be carefully examined. It should have a fine rose colour, and be perfectly soluble in warm water, leaving no black residue. In case this is observed, which happens only when the heat has been too high, a drop of sulphuric acid and a few drops of oxalic acid may be added, and the whole evaporated to dryness and again ignited. When, however, there is much oxide of cobalt present, it is better to reject the analysis at once. With a little care and practice the operation succeeds almost invariably, and the result, as we

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shall hereafter show, leaves nothing to be desired in point of accuracy. When chlorine is present in the salt to be analysed, a little free chlorine is sometimes found among the products of the action of the sulphuric acid, and the platinum crucible is slightly acted upon. In such cases we usually add a little oxalate of ammonia to the salt before dropping the acid upon it. The quantity of salt to be taken for analysis may vary from 3 to 5 decigrms.; when more is used, there is apt to be some loss from effervescence. In consequence of the small quantities of substance employed, the weighings must be as accurate as possible. In calculating the weight of the cobalt from that of the sulphate, we have the advantage of determining one substance from another with an equivalent more than twice as high.

In certain cases, as for example when phosphoric acid, chromic acid, &c. are present, the above method cannot be employed. In such compounds we have found it advantageous to separate the cobalt as a hydrate of the sesquioxide, by boiling the salt with a solution of caustic potash, washing the precipitate thoroughly, and estimating the ignited precipitate as $Co^6 O^7$, or as metallic cobalt after reduction by hydrogen. Fremy justly observes that this ignited oxide usually contains potash; but an accurate result may always be obtained by washing it well with boiling water after the ignition and weighing a second time. It is remarkable that Fremy asserts that cobalt may be accurately estimated in the form of sulphate, in consequence of the stability of this salt, while the direct application of the method, as we have described it above, appears to have escaped him entirely.

Hydrogen.—We have in almost all cases determined hydrogen directly by combustion with chromate of lead, metallic copper being placed in the anterior part of the tube. In the case of the nitrates, however, an excess of hydrogen in the result is almost unavoidable, because it is impossible, even with freshly reduced copper, to decompose completely the great quantity of oxides of nitrogen formed during the combustion. In other cases this effect is much less marked, and the hydrogen determinations are at least as accurate as in ordinary organic analyses.

Chlorine.—The accurate determination of the chlorine in the ammonia-cobalt salts is very difficult. Nitrate of silver, it is true, precipitates chlorine from most of its combinations in these salts; but the precipitation is never complete, because the chloride of silver is somewhat soluble in the ammonia-cobalt chlorides, forming with them peculiar double salts. By long boiling, with free nitric acid in the solution, nearly all the chlorine may be determined as chloride of silver, but very accurate results cannot be obtained in this manner. The best method consists in igniting the chloride with lime in a combustion-tube in the manner usually practised with organic bodies. In some cases, however, we have obtained very good results by decomposing the solution of the chloride by sulphurous acid, or by boiling the solution of the salt until it is completely decomposed, adding sulphurous or nitroso-nitric acid to reduce the sesquioxide

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of cobalt, and then precipitating with silver. The process is, however, always troublesome, and requires much time and great care.

Carbon.—This element is best determined by the usual process of organic analysis. In consequence, however, of the very large quantity of oxides of nitrogen, which are always produced during the combustion of these salts, we have found it very advantageous to employ a method first suggested, we believe, by Winkelblech, and which consists in mixing with the oxide of copper a quantity of finely-divided metallic copper, in the form in which it is obtained by reducing the oxide by hydrogen. In this manner the formation of the oxides of nitrogen may be completely prevented. Great care must, however, be taken when it is wished to determine hydrogen at the same time with carbon, because copper reduced from the oxide by hydrogen always contains water, which it is difficult to separate.

Nitrogen.—No element has presented such difficulties as nitrogen. We have found it impossible to obtain results within 2 or 3 per cent. of the truth by employing the old methods of analysis, that of Dumas for instance. The quantity of nitric oxide formed during the combustion is surprising, and it is absolutely impossible to get rid of it by means of ignited metallic copper, placed in front of the combustion-tube. Will and Varrentrapp's method with soda-lime is inapplicable, because 1 equiv. of ammonia is always decomposed by the equivalent of oxygen set free in the reduction of sesquioxide to protoxide of cobalt. Good results could not be obtained by boiling the salts with caustic alkalies, collecting the ammonia in hydrochloric acid, and determining it by bichloride of platinum. Even after the reduction of the sesquioxide of cobalt to protoxide by means of sulphurous acid, this method was found unreliable. The improvements made by Simpson in the absolute determination of nitrogen by volume at last furnished us with a reliable process, and nearly all the analyses in this memoir were executed by his method. The improvement introduced by Simpson consists essentially in mixing oxide of mercury with the oxide of copper employed to effect the combustion. The vapour of metallic mercury completely decomposes the oxides of nitrogen, and any excess of free oxygen is absorbed by means of metallic copper. By this method we have analysed most of our compounds without special difficulty, though we have often found it necessary to employ a much larger proportion of oxide of mercury than is recommended by Simpson. One class of ammonia-cobalt bases have, however, been the source of frequent analytical failures, and of great loss of time and material. We refer to the salts of xanthocobalt, a base containing deutoxide of nitrogen, and giving off this gas at a gentle heat, below that at which oxide of mercury is decomposed. Simpson's method has not always been found accurate, since even when a very large amount of oxide of mercury is employed, there is frequently much nitric oxide in the nitrogen collected for measurement. In many cases the simple admixture of a large proportion of metallic copper with the oxide, as recommeded by Winkelblech, has been found to give most excellent results. It is proper also to state here, that in consequence of diffi-

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culties in obtaining proper apparatus, with which European chemists do not have to contend, we have, in the majority of cases, measured the volume of nitrogen in the old way, using however very accurately graduated tubes for collection, and correcting with great care for temperature and pressure. We have also found it advantageous to operate upon quantities of substance sufficient to yield at least 200 cub. centims. of gas, since in this way the error of reading becomes extremely small.

Sulphuric Acid.—This acid cannot be accurately determined in the ammonia-cobalt salts by direct precipitation with chloride of barium. In almost all cases a great apparent excess of acid is obtained, and this may amount to 5 per cent., even when the sulphate of baryta appears to have been completely washed. We have therefore in all cases preferred to decompose the salt to be analysed, by boiling it with a little ammonia. After complete precipitation of the sesquioxide of cobalt, hydrochloric acid is to be added to reduce and dissolve the oxide, when the sulphuric acid may be directly thrown down by chloride of barium. Even with these precautions, our results are not unfrequently two-tenths or three-tenths of one per cent. too high, almost never too low.

Oxalic Acid.—The ordinary methods for the quantitative estimation of this acid fail entirely with the class of salts under consideration. A solution of terchloride of gold is reduced only after very long and tedious boiling, and then incompletely. Even after previous reduction of the cobalt to the form of protoxide, the method is found to be very inconvenient and inaccurate. The conversion of the oxalic into carbonic acid by oxidation, and its determination from the weight of this last, gave no better results, inasmuch as the oxidation is effected with difficulty. We have therefore in all cases had recourse to ultimate organic analysis, which alone gives reliable results.

The methods employed in the determination of other substances will be described, when necessary, in treating of the particular compounds.

Roseocobalt.

The description of the salts of roseocobalt forms, upon the whole, the most convenient starting-point in a statement of the results of our investigation. These salts are in general easily obtained, and the products of their decomposition include several of the other bases, which we shall have occasion to describe. They are almost all well crystallized, and are in general nearly insoluble in cold water, soluble without decomposition in warm water slightly acidulated, but easily decomposed when the neutral solutions are boiled, a hydrated hyperoxide of cobalt being thrown down, while free ammonia is given off. The salts of roseocobalt have a purely saline, not metallic taste; their colour varies, being sometimes dull or brick-red, and sometimes cherry-red. They are usually dichrous, though a few of them do not exhibit this property in a marked degree. Heat decomposes the dry salts readily, the final products

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of the decomposition being usually ammonia, a salt of ammonium, and a salt of protoxide of cobalt. Intermediate products are, however, sometimes formed, as we shall hereafter see. Thus in many cases the salts of roseocobalt on boiling yield salts of luteocobalt, which by continued boiling are completely decomposed. The salts of roseocobalt may almost always be prepared by the direct oxidation of ammoniacal solutions of salts of protoxide of cobalt; but the particular circumstances which accompany the formation of each one will be best considered in treating of the separate compounds. Roseocobalt is a triacid base.

[To be continued.]

On the Action of Iodide of Æthyle upon Tungstate of Silver.

By A. GÖSSMANN.

The preparation of a compound of oxide of æthyle and tungstic acid has not yet been effected. Neither the heating of the sulphuric acid salts of oxide of æthyle with compounds of tungstic acid, nor the action of perchloride of tungsten upon alcohol, have furnished the desired result, although these methods have effected this object with some acids nearly allied to tungstic acid. The behaviour of oxide of silver and its compounds to iodide of æthyle led the author to think it probable that a compound of oxide of æthyle, with tungstic acid would be produced by the action of iodide of æthyle upon tungstate of silver. The ease with which water could be excluded, and the property possessed by both compounds of bearing exposure to a pretty high temperature without one being decomposed before the other, appeared to support this opinion. This supposition, however, was contradicted by the results of repeated experiments, in which the author obtained iodide of silver, free tungstic acid, and oxide of æthyle.

If dry tungstate of silver, prepared by precipitating tungstate of ammonia with nitrate of silver, be mixed with an excess of rectified and well-dried iodide of æthyle in a vessel capable of being well closed, the mass becomes strongly heated in a few minutes, and at the same time acquires a yellow colour. If the contents of the vessel be examined some hours afterwards, they are found to consist of the excess of iodide of æthyle, free tungstic acid, and iodide of silver. If the experiment be altered by employing a slight excess of the silver salt, and the vessel be opened after some days, the characteristic odour of pure oxide of æthyle (æther) is perceived; the pulverulent dried contents, when heated, become brownish-yellow, without giving the slightest indications of containing organic matters; on cooling they again become yellow, and furnish to dilute ammonia all the tungstic acid, and the residue of tungstate of silver, whilst iodide of silver remains undissolved. To obtain this result it is necessary to continue the action for some days, and by frequent agitation to assist the contact of the iodide of æthyle, which is diffused in the vessel in a gaseous form, with the silver salt.—Liebig's *Annalen*, February 1857, p. 218.

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On a new Series of Oxygenated Artificial Bases. By S. Cloez.

The number of artificial tertiary bases has increased considerably in the last few years, but we hardly know ten oxygenated alkaloids prepared artificially in our laboratories. The production of bodies of this kind is however interesting in several respects, first in a purely chemical point of view, and secondly, as it may lead one day to the œconomical preparation of some substances of great value in medicine, which are now obtained at great cost from natural products.

The low price of sodium allows it to be employed as a reagent in laboratories; its action upon the different alcohols gives rise to perfectly definite compounds, capable of conversion by double decomposition or by substitution into new bodies, most frequently of unforeseen nature. Thus most of the compound æthers may be obtained by the mutual action of sodium alcohol and the chloride corresponding to the acid which it is desired to unite with the æther. Æthylate of soda, for example, treated with chloride of benzoyle, gives benzoic æther and chloride of sodium; the reaction takes place in accordance with the equation

$$C^{14} H^5 O^2 Cl + C^4 H^5 NaO^2 = NaCl + C^{14} H^5 O^3, C^4 H^5 O.$$

With the same compound and the chlorosulphuret of phosphorus the author recently obtained neutral sulphophosphoric æther:—

$$PCl^3 S^2 + 3(C^4 H^5 NaO^2) = 3(NaCl) + PO^3 S^2 3(C^4 H^5 O).$$

The substitution of oxychloride of phosphorus for the sulphochloride, furnishes neutral phosphoric æther:—

$$PCl^3 O^2 + 3(C^4 H^5 NaO^2) = 3NaCl + PO^5 3(C^4 H^5 O).$$

The author has attempted to produce cyanic and cyanuric æthers by the action of gaseous, liquid, and solid chlorides of cyanogen upon sodium alcohol; a reaction took place, but the products differed completely from what he expected.

When gaseous chloride of cyanogen is passed slowly into a solution of æthylate of soda in absolute alcohol, the gas is rapidly absorbed, an abundant white deposit of chloride of sodium is formed, and at the same time the temperature of the mixture is greatly elevated; after the reaction, the chloride of sodium is separated by filtration, and the filtrate distilled in the water-bath to drive off the alcohol and the excess of chloride of cyanogen. The residue is a syrupous liquid with a slight deposit of chloride upon the walls of the retort; it differs in all its properties from cyanic æther. It is almost inodorous, and is not volatilizable without decomposition; most acids dissolve it and form crystallizable compounds; hot concentrated potash decomposes it, with evolution of ammonia, but without producing æthylia; its only character in common with cyanic æther is its insolubility in water, which allows it to be freed from traces of chloride of sodium by washing, and it is afterwards dried with facility by exposing it for twenty-four hours *in vacuo* over sulphuric acid.

The most simple formula arrived at by the analysis of the body

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thus purified is that of cyanogen alcohol, isomeric but not identical with cyanic æther:—

$$C^6 H^5 NO^2 = C^4 \left(\begin{matrix} H^5 \\ Cy \end{matrix}\right) O^2 = C^4 H^5 O, CyO.$$

The formation of this new body, *cyanætholine*, is easily understood; it takes place in accordance with the equation—

$$C^4 \left(\begin{matrix} H^5 \\ Na \end{matrix}\right) O^2 + CyCl = NaCl + C^4 \left(\begin{matrix} H^5 \\ Cy \end{matrix}\right) O^2 = C^6 H^5 NO^2.$$

Cyanætholine, with the analogous bodies furnished by the different alcohols, belongs to a new series parallel to that of glycocol, alanine, leucine, &c. These two series are very closely allied; the chemical properties of their respective corresponding terms are similar; if we know the one, we may divine the others almost with certainty.

Cyanætholine is a slightly coloured liquid, of an oily appearance. Its density is =1·1271 at 59° F.; it has a slightly bitter taste, followed by a very disagreeable persistent acridity; its odour is very slight, and resembles that of oil of wine; when heated in a retort, it is decomposed into a colourless volatile liquid and a black carbonaceous residue.

It is insoluble in water, but mixes in all proportions with alcohol and æther; hot concentrated potash decomposes it; it dissolves in muriatic acid, with which it forms a crystalline muriate, capable of combining with bichloride of platinum to form a yellow double salt. The sulphate forms small prismatic crystals when the solution of the base in sulphuric acid is left to spontaneous evaporation.

The nitrate forms a double salt with nitrate of silver; this compound is obtained in pretty large crystals by mixing a dilute solution of nitrate of silver with a dilute solution of cyanætholine in a slight excess of nitric acid.

The nitrous acid produced by passing deutoxide of nitrogen into the solution of cyanætholine in nitric acid, converts this substance into a solid and crystallizable acid matter; the reaction takes place, as with alanine, with an effervescence due to an evolution of nitrogen. The acid produced was not analysed, from an insufficiency of material. It will be curious to see whether it is not isomeric with acrylic acid, or rather a homologue of maleic or fumaric acid. If these views be confirmed, the latter acid may perhaps be produced artificially by starting from methylic alcohol, and passing successively through metholate of soda and cyanætholine.—*Comptes Rendus*, March 2, 1857, p. 482.

On the Behaviour of Carbonic Acid to the Organic Bases and to some Sesquioxides. *By* M. Langlois.

Some years ago, the author showed that organic bases, such as quinine, are capable of combining with carbonic acid under certain circumstances. He has now tested strychnine, brucine, veratrine, and morphine, as regards their behaviour towards carbonic acid.

These bases dissolve more abundantly in water saturated with

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carbonic acid than in pure water; they crystallize therefrom, however, without retaining any carbonic acid. Veratrine alone has a somewhat greater affinity for carbonic acid; the surface of the solution in carbonic acid becomes covered with a film of crystals, which contain water and carbonic acid. When dried at the ordinary temperature of the air, however, they lose their water and carbonic acid. By the mutual decomposition of one of their salts and an alkaline carbonate, they are all thrown down free from carbonic acid.

Hydrated alumina takes up no carbonic acid in a current of carbonic acid. The precipitate thrown down by means of an alkaline carbonate at the ordinary temperature, which is generally regarded as hydrated alumina with a residue of alkaline carbonate, loses all alkali by sufficient washing, and then still retains 7·72 per cent. of carbonic acid. This precipitate therefore is not a pure hydrate. Its analysis gave—

Al^2O^3	48·80
HO	43·48
CO^2	7·72

At a temperature a little above 212° F. the precipitate loses the carbonic acid. According to this, its constitution is $3(Al^2O^3, CO^2) + 5(Al^2O^3, 8HO)$. Hydrated oxide of iron takes up no carbonic acid from water saturated with carbonic acid. The precipitate thrown down by an alkaline carbonate from a salt of oxide of iron and freed from all alkali, still always contains carbonic acid, which is not eliminated at 212° F., but only at 329° F. The precipitate, dried at 212° F., had the following composition:—

Fe^2O^3	88·47
CO^2	1·36
HO	10·17

An alkaline carbonate throws down a precipitate from neutral salts of oxide of chrome, the composition of which, as Berzelius states, is $Cr^2O^3, CO^2 + 3(Cr^2O^3\,HO)$. The author obtained a precipitate of a different composition, which, like the iron precipitate, only lost its carbonic acid at 329° F., and after being dried in the water-bath, gave on analysis—

Cr^2O^3	67·43
CO^2	10·51
HO	22·06

According to this it has the constitution—

$$Cr^2O^3, CO^2 + Cr^2O^3 + 6HO.$$

Ann. de Chim. et de Phys., 3 sér. xlviii. p. 502.

On Amylic Alcohol. *By* M. Schlagdenhauffen.

If potato fusel-oil be distilled in the presence of water and chloride of lime, chloroform is obtained. 130 grms. of oil, 400 grms. of

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chloride of lime, and 800 grms. of water furnished 18 grms. of chloroform. In another experiment with 250 grms. of oil, 2 kilogrms. of chloride of lime, and 7 litres of water, 50 grms. of chloroform were obtained. The reaction is not so violent as when chloroform is prepared with ordinary alcohol and chloride of lime. The chloroform obtained from potato fusel-oil is identical with that prepared from alcohol.

Chloride of phosphorus, PCl^3, acts very violently upon amylic alcohol, but the reaction is not so stormy as when the æther of this alcohol is treated in the same way. Acetate of oxide of amyle may be mixed with chloride of phosphorus; the temperature rises but little, and when benzoate of oxide of amyle is employed, nothing of the kind is observed.

The author enclosed a mixture of an excess of acetate of oxide of amyle and protochloride of phosphorus in a glass tube, heated it for six hours in the oil-bath, and afterwards for two hours longer to 356° F.; he then examined the products of decomposition. It appeared that the reaction takes place here in accordance with the equation—

$$3C^4H^3O^3, C^{10}H^{11}O + 2PCl^3 = 2PO^3 + 3C^4H^3O^2Cl + 3C^{10}H^{11}Cl.$$

Chloride of acetyle, chloride of amyle, and phosphorous acid are formed in the above proportions.

When benzoate of oxide of amyle was treated in the same way in the oil-bath at boiling-heat for eight hours in sealed tubes with the chloride of phosphorus in excess, phosphorous acid, chloride of amyle, a small quantity of chloride of benzoyle, and some benzoic acid were formed. The decomposition in this case may be expressed by the following equation:—

$$3C^{14}H^5O^3, C^{10}H^{11}O + 2PCl^3 = 2PO^3 + 3C^{14}H^5O^2Cl + 3C^{10}H^{11}Cl.$$

In a second experiment of the same kind, other products of decomposition were obtained; the oxide of amyle alone had become decomposed, and produced phosphorous acid and chloride of amyle, whilst the anhydrous benzoic acid remained, having become less attackable under such circumstances. This second phase of the decomposition may be expressed as follows:—

$$3C^{14}H^5O^3, C^{10}H^{11}O + 2PCl^3 = 2PO^3 + 3C^{14}H^5O^3 + 3C^{10}H^{11}Cl.$$

Amongst *reducing bodies*, the solution of protochloride of iron at 176° F. acts especially upon nitrite of oxide of amyle. The mixture becomes brown, and soon deposits peroxide of iron; nitrous oxide gas is evolved, produced by the decomposition of the nitrous acid. If the protacetate of iron be employed instead of the protochloride, the oxidation goes further. Nitrous acid and water are reduced so far, with formation of undissolved peroxide of iron, that only nitrogen and hydrogen remain, which combine to form ammonia:—

$$12(C^4H^3O^3, FeO) + 3HO + NO^3, C^{10}H^{11}O = 12(C^4H^3O^3, Fe^2O^3) + C^{10}H^{11}O + NH^3.$$

Ammonia and nitrous oxide gas are also obtained when nitrate of oxide of amyle is reduced with protochloride or protacetate of iron.

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Iron filings and acetate of iron together also produce these two bodies at the same time; protacetate of iron converts all the oxides of nitrogen into ammonia. Metallic iron consequently reduces nitric æther more completely than protochloride of iron, and protacetate of iron again reduces it still further than metallic iron.—*Journ. de Pharm. et de Chim.*, 3 sér. xxx. p. 401.

On the Composition of the Bronze of ancient Egyptian Statuettes. By M. Chevreul.

During a residence of four years in Egypt, Mariette, as is well known to archæologists, has done peculiar service to the study of the antiquities of that country. Amongst his discoveries, and the treasures with which he has enriched the collection at the Louvre, are some bronze statuettes which were found at a depth of some centimetres beneath the soil, and in all the vaults of the Serapeum.

It appears that the ancient Egyptians buried these statuettes with the view of purifying the sand, which, according to their ideas, was impure, and which was incessantly disturbed by the feet of the people who visited the Serapeum. Hundreds of such statuettes were brought to France by Mariette; their size varies from a few centimetres up to 80 centimetres in height. They are covered with a coat of verdigris of variable thickness. The author has examined their mass.

1. *Hollow Statuettes.*—The cavities of these are filled with a white or coloured earth. The white earth is essentially basic carbonate of lime with some clay; it also contains large quantities of chloride of sodium, chloride of calcium, and sand-grains. The coloured earth consists essentially of carbonate of lime and clay: it contains oxides of copper and iron, and a residue insoluble in nitric acid, containing silica, protoxide of iron, and alumina.

The interior of the hollow statuettes also contained another matter very different from the earthy substances; it was fused, and adhered firmly to the bronze. It consisted of litharge and basic carbonate of lead, and contained arseniate of lead.

2. *Gilt Statuettes.*—The gold is attached to the hollow statuettes in two different ways,—*a.* by damaskening, and *b.* by a white material with which the bronze is coated, and upon which a leaf of gold is fixed. This coating is not gypsum, as has been supposed, but a very finely divided carbonate of lime, mixed with an organic substance.

Composition of the hollow and massive Statuettes.—Both consist of a very excellent bronze, which occurs in four different states, namely,—

A. As a green layer, which appears blue in some spots.

B. As a blood-red mass.

C. As reddish bronze.

D. Of the appearance of ordinary unaltered bronze.

The form A. is bronze in the highest state of atmospheric decomposition; the coatings of the statuettes also consist of this. It consists of a definite compound of perchloride of copper with oxide

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of copper and water, in the proportions of the oxychloride of copper from Peru. The blue portions contain water, carbonic acid and oxide of copper; they are the blue hydrated carbonate of copper.

B. The blood-red material consists principally of protoxide of copper mixed with protoxide of tin. Some chlorine occurs in it, in many cases in considerable quantity, apparently forming protochloride of copper.

C. The reddish bronze appears to have been produced in consequence of its tin having been more altered than its copper.

D. The well-preserved bronze is remarkable for its excellent properties.

Reproduction of a Statuette which was almost entirely decomposed.—The author placed a statuette of this description in a porcelain tube, and heated it to redness in a current of hydrogen. Water and some muriatic acid containing copper passed over; the figure itself was completely restored.

The sand in which these figures were discovered contains soluble chlorides, produced by the action of water containing chloride of sodium upon lime; these have transformed the bronze into the above compounds. The aqueous extract also contained some carbonate of soda.

Copper and tin have thus gradually become converted into perchlorides, oxides, and carbonates from the surface inwards; the tin has been converted into oxide; the outermost layer of the copper has also been converted into oxide and perchloride, whilst at the point of contact with the unaltered bronze in the interior it has only been able to become oxidized to the state of protoxide.

In a crack in one statuette the author found crystals of blue basic carbonate of copper, chloride of lead, and hydrated oxychloride of copper (*cuivre muriaté*).

If the bronze of the statuettes be dissolved in nitric acid, oxide of tin containing arsenic is left.—*Comptes Rendus*, xliii. p. 733 & 989.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Detection of the Adulteration of Essential Oils, especially with Oil of Turpentine. By G. S. Heppe.

It is remarkable that well-dried nitroprusside of copper behaves in a very characteristic manner towards oil of turpentine and some other oils, so that this reagent may serve for the detection of oils free from oxygen, especially oil of turpentine, in those which contain oxygen. Turpentine cannot be detected by this means in oils which are themselves free from oxygen, such as oil of lemons, oil of orange, or oil of juniper.

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A fragment of nitroprusside of copper, of the size of a pin's head, is brought in contact with a small quantity of the oil to be tested in a test-tube; it is heated until the oil begins to boil, kept boiling only for a few seconds, and then allowed to settle. If the oil be an oxygenated oil free from turpentine, the nitroprusside of copper becomes black, brown or gray, and the supernatant oil changes its colour and usually appears darker. If the oil contains turpentine, the deposit is of a fine green, or bluish-green, and the supernatant oil colourless or slightly yellow.

The above-mentioned conditions must be exactly observed. If necessary the lens must be employed to ascertain the changes of colour, for even the colour of nitroprusside of copper treated with oil of turpentine is different and more intense than its original colour. Sometimes also it is advisable to make experiments with pure oil.

Of the oils free from oxygen the author investigated the following, and found their action the same as above described, even when the boiling was continued longer; it was only in No. 7 *a* and *e* that the oil became darker, but the deposit was of a more intense green.

1. Petroleum, crude and rectified; 2. Oil of bitter oranges; 3. Oil of sweet oranges; 4. Oil of orange flowers; 5. Oil of juniper berries; 6. Oil of savin; and 7. Oil of turpentine: *a*, crude German; *b*, crude French; *c*, rectified French; *d*, German rectified over lime; and *e*, very old, rectified French, which had become thick.

The oils containing oxygen behave similarly in general, but even here small differences occur. Of the oils from the *Umbelliferæ* the author tested,—

1. *Oleum Carui*, prepared from the seeds and from the stalks, pure and mixed with oil of turpentine. The pure oil, when boiled with the reagent, rapidly became turbid; the precipitate was deposited with difficulty; the change of colour was more distinct the longer the boiling, and the older the oil. An addition of oil of turpentine entirely prevented the decomposition, but it must not be boiled too long, as oil of turpentine is more volatile than the other essential oils.

The oil from the stalks, which is of a less agreeable odour, behaved when pure exactly like the oil of the seeds. Nearly all the samples obtained from different manufactories contained oil of turpentine.

2. *Oleum Fœniculi.*—The reagent became first dark green and then black; with a very small quantity of the reagent the oil became brownish-yellow, with a larger quantity reddish-brown. In this case the author believes that 20 to 22 parts of oil decompose 1 part of the reagent. The addition of oil of turpentine prevented the decomposition.

3. *Oleum Anethi*, and 4. *Oleum Anisi semin.* exhibit the reaction very rapidly; weaker when 1 part of the nitroprusside of copper is acted upon by 1000 parts than by 100 parts of the oil: the deposit is black.

5. *Oleum Cumini semin.* became brownish-yellow with the first,

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and dark yellowish-brown with the second proportion: the deposit was only ashy-grey.

Of the oils of the *Labiatæ*, the author examined,—

6. *Oleum Lavandulæ.*—It furnished a slate-gray deposit. The colour of the oil became darker according to the quantity of the reagent.

Also 7. *Oleum Menthæ pip.*; 8. *Oleum Menthæ crisp.*; 9. *Oleum Melissæ*; 10. *Oleum Majoranæ*; 11. *Oleum Salviæ*; 12. *Oleum Serpylli.* They behaved in general like *Oleum Lavandulæ.* With some the deposit was quite black; with others brown or greyish-black. An addition of oil of turpentine prevented the change of colour.

Of the oils of the *Compositæ*, there were tested,—

13. *Oleum Absinthii*; 14. *Oleum Cynæ*; 15. *Oleum Millefolii flor.*; and 16. *Oleum Tanaceti.* With these the deposit was rather brownish-black, and only pure black with *Oleum Cynæ.* The beautiful blue colour of the *Oleum Absinthii* became first pale blue, and then dark green.

The author also examined the following oils from the *Myrtaceæ*:—

17. *Oleum Cajeputi*, the green colour of which became brownish-yellow: the deposit was black.

18. *Oleum Caryophyllorum.*—The crude and rectified oils were boiled with the reagent; the colour of the oil became violet and cherry-red, and the deposit was slate-gray. Even $\frac{1}{2000}$ of the reagent produced a rose colour. Oil of turpentine also prevents the action, when it is not entirely driven off by too strong a heat.

From the *Laurineæ*, 19. *Oleum Cassiæ*, and 20. *Oleum Sassafras*, were treated in the same way: in both the reagent became black, the colour of the oil was rendered darker; the reagent became opake, and the oil separated into two strata.

21. The *Oleum Anisi stellati* of the family *Magnoliaceæ* also gave a black precipitate; 22. *Oleum Valerianæ* (*Valerianaceæ*) behaved in the same way. Of the *Rutaceæ*, only 23. the *Oleum Rutæ graveol.* was tested; the deposit was ash-grey; the oil was pale yellow and became brownish-yellow.

24. *Oleum Bergamottæ*, of the family *Hesperideæ*, when pure gave an ashy-grey deposit and acquired a darker colour. The addition of oil of lemons entirely prevented the reaction.

Of the *Monocotyledones*, only 25. the *Oleum Calami radicis* was tested: it furnished a slate-gray or black deposit, and became dark reddish-brown.

Oleum Sinapis and *Oleum Amygdalarum amar.*, of which the author thinks it questionable whether they are to be reckoned amongst the essential oils, behave towards the reagent in the same way as the oils free from oxygen; the colour of the nitroprusside of copper becomes a beautiful dark green.

The chemical nature of the changes produced by this reagent could not be ascertained with certainty.—*Zeitch. für Pharm.* 1856, Nos. 6, 7, 8. *Archiv der Pharm.* cxxxix p. 57.

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On Soluble Glass, its Preparation and Applications.
By J. N. von Fuchs.

[Continued from page 140.]

Applications of Soluble Glass.

Undoubtedly one of the most useful applications of soluble glass is to painting, as it is peculiarly fitted to fix colours well, and also to give great permanence to all coatings. This mode of painting is called *stereochromy* by the author; and under this term he understands those methods of painting in which soluble glass constitutes the medium for fixing the colours and their supports, in which respect stereochromy is essentially distinguished from all other kinds of painting.

In monumental painting it competes with fresco-painting, and will undoubtedly supersede it, and even attain a wider field of application. In Prussia fresco-painting has already been given up to a great extent, and the wall-pictures in progress there are being executed by the stereochromic process. In England also this method has met with great acceptance. The so-called encaustic painting cannot compare with it.

The author was first led to the idea of employing soluble glass in painting by the numerous complaints of the imperfections of fresco-painting, and the general opinion that frescoes would not last in our climate. He met with great difficulties in effecting the application of soluble glass to this kind of painting, and only succeeded when he united himself with Von Kaulbach for this purpose.

Wall or Monumental Painting upon a Mortar-ground.—When a stereochromic picture is to be applied in a beautiful and permanent manner to a wall, especial care must be devoted to the material to which the work of art is to be applied, that is to the mortar, the substratum, and the superstratum. Errors made in this may render the painting difficult, and injure the beauty of the pictures. In this, the principal problem is to give the ground an equal stony solidity throughout, and as it were to amalgamate it with the wall, but at the same time to manage that it imbibes the soluble glass well and uniformly in all parts. The first coat, or substratum, is made with ordinary lime-mortar, so as to do away with the inequalities of the wall, and cover the stone well. The sand in this should be of a medium size, neither too coarse nor too fine; it is, however, of little consequence whether it be calcareous or quartz-sand, but either must be well washed before use. The properly-slaked lime must be sparingly employed, in order that the mortar, which is to be made with distilled or rain-water, may be rather poor than fat. If the mortar were too fat, the soluble glass would penetrate with difficulty, and would also form cracks here and there, which are to be avoided.

The plaster thus prepared must not only be allowed to dry well, but must also remain exposed for several days to the air, in order that it may attract carbonic acid and become converted into subcarbonate of lime; for if the lime in this mortar were still caustic, the

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soluble glass would be decomposed by it, and could not penetrate into the wall, which is extremely necessary if a good binding is to be effected by it.

To facilitate the impregnation of the lime with carbonic acid, a solution of carbonate of ammonia may be employed, by which the mortar acquires a greater solidity when it has been moistened with it two or three times. When it has again become quite dry and the ammonia has evaporated, the soluble glass is employed to fix it and attach it firmly to the wall; with this it is to be well soaked repeatedly, drying between each application, until it is almost saturated. The soluble glass employed for this purpose should be soda- or double water-glass, mixed with so much solution of silicate of soda that it may be quite clear, and not opalescent.

Soda-glass or double water-glass is to be preferred to potash water-glass, because it is absorbed better. It is not to be employed in a concentrated state, but diluted with an equal volume of water, as otherwise there is a probability that it would not penetrate into the wall. As the plaster cannot be equally thick in all parts on account of the inequalities of the wall, and the thicker parts require more soluble glass than the thinner, and consequently continue to absorb it when the latter are already saturated, the thick parts must be sought out with a moist brush, and soaked with soluble glass until they are saturated.

When the substratum is fixed in this way, the superstratum, which is to receive the picture, may soon afterwards be applied. As already stated, much depends on this being of the proper nature, if the desired object is to be attained with certainty and without difficulty.

For this purpose, the superstratum, which does not differ essentially from the substratum, should be prepared with distilled or rain-water and well-washed sand (calcareous or quartz-sand), of a particular grain, not exceeding a certain size, and kept rather poor, in order that it may not form any cracks and may be able to absorb readily. To get the sand of the proper grain, it must be passed through a sieve, such as is known in Munich as No. 9, and the meshes of which measure five Rhenish points in width.

As regards the quality of the calcareous sand, that which is artificially obtained by pounding marble or dolomite is to be preferred to natural sand, because the latter consists of roundish, and as it were ground grains, which do not bind so well as the sharper granules of the artificial calcareous sand, which possess a fresh and rough surface. The very fine powder, which is however advantageous for good binding, must be got rid of either by lixiviation or by a fine sieve, as otherwise the mass would be rendered too compact and no longer thoroughly absorbent.

The texture of the surface of the painting-ground depends principally on the size of the grains of sand; the coarser these are, the rougher will it turn out, which to a certain extent is favourable to the painting so long as the colours, which are to be applied merely with water, adhere sufficiently until the application of the soluble glass.

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The surface should never be smooth or ground, because then it receives but little or none of the colour without fixing media. As Von Kaulbach expresses himself, the surface must feel like a file. A distinction must also be made between pictures which are to be seen closely and those which are to be viewed from a distance; in the latter the grain of the surface may be considerably coarser than in the former, for which rather finer sand should be used.

This ground or mortar is applied as evenly as possible to the thickness of about a line upon the substratum; and when it has become dry, it is rubbed with a sharp sandstone (or, as in Berlin, with an iron ruler), in order to give the surface the proper roughness, and at the same time to remove the thin stratum of carbonate of lime formed during desiccation, which would prevent the absorption of the soluble glass.

The author, however, considers it far better to destroy the incrustation by a simple chemical agent, namely dilute phosphoric acid (1 part of concentrated acid to 6 parts of water). A sponge soaked with this fluid, or a brush moistened with it, passed over the surface, does all that is necessary. As the phosphate of lime thus produced binds well with soluble glass, no injury is done to the mortar thereby, and at the same time we avoid the starting of small fragments, which may take place during the mechanical rubbing, forming small holes which require to be repaired.

When the ground is so far prepared and well dried, it is impregnated with soluble glass, in order to give it the necessary consistency and amalgamate it properly with the substratum. For this purpose, double soluble glass, rendered clear by silicate of soda and diluted with an equal quantity of water, may be employed with advantage. It will generally be sufficient to perform this operation twice, drying the mass after each application, for it must be done in moderation in order that the pores may not be closed by too much soluble glass, by which the difficulty of the painting would be considerably increased. If a mistake has been committed in this respect, the ill effects can only be got over, either by removing the mortar, or by waiting for a time before commencing the painting, until by the further contraction of the soluble glass the ground opens again of itself. This will be greatly facilitated by heat, which is most easily applied by burning spirit of wine upon the ground.

After the superstratum has been prepared either by friction or phosphoric acid, and fixed with double soluble glass to which a little silicate of soda has been added in such a way that this has been uniformly diffused over its surface, and the ground has proved to be uniformly and thoroughly absorbent, the painting may be commenced. There is, however, no occasion to hurry with this; on the contrary, it is even well to wait for a time, because in the meanwhile the ground becomes drier, and thus the faculty of absorbing, which is absolutely necessary for the painting, is increased.

The colours are applied with pure water; and the wall is frequently syringed with pure water, in order to expel the air from its pores and assist the adhesion of the colours. This syringing, how-

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ever, should be moderate, and no more than is necessary, and the greatest possible care should be taken that the neighbouring parts, which are already painted, may not receive too much of it, because otherwise, as Echter remarks, the colours would lose somewhat in brilliancy; the reason of which apparently is, that by the application of too much water the finest and weakest colouring particles are washed up on the surface, and thus separated from the other more powerful ones. This undesirable result occurs especially on those places which are repeatedly painted over, and for this purpose require to be moistened. Echter, however, has found a means of entirely getting rid of this inconvenience, by brushing off these dull colouring particles, after drying and before fixation, by means of a very fine brush, after which the colours again make their appearance in their original purity.

Nothing more is then necessary than to fix the colours properly, for which purpose the soluble glass for fixing has already been indicated (at p. 132) as peculiarly applicable. It is sufficient to dilute it with one-half of water.

As, however, the colours only adhere weakly, and do not allow of the use of the brush, the soluble glass must be syringed upon them in the form of a very fine rain or cloud, and at first very cautiously, in order that the colours may not be removed from their places and run together. For this purpose, Prof. Schlotthauer, who has occupied himself much with stereochromic experiments, has invented a syringe which scarcely leaves anything to be desired. This operation is continued, with intervals of drying, until the colours adhere so firmly that they communicate nothing to the fingers when passed over them. When white pocket-handkerchiefs, which are sometimes used for this purpose, are dirtied by strong friction, this proves nothing against the permanence of the colours, because when rubbed with a strong pressure grains of sand are loosened, and these attack the colours, which however the pocket-handkerchiefs cannot do of themselves. The same thing may also be observed in fresco-paintings.

In testing the colours as to their permanence and fixity, it is sometimes found that whilst some of them are sufficiently fixed, others still appear to be more or less loose, and dirty the fingers. To these belong the so-called meagre colours, such as black. These require still more soluble glass, which must be applied to them by means of a fine pencil, until they adhere as firmly as the others. Von Kaulbach, however, has very recently stated that this occurs very rarely, as it may be obviated by a proper mixture of the colours.

This is essentially the process by which Von Kaulbach, assisted by Echter, has executed four large stereochromic pictures in the new Royal Museum at Berlin, as to the excellence of which, especially the last, there is but one opinion.—*Abhandl. der Naturw. Commission bei der Konigl. Akad. der Wiss. zu München*; Dingler's *Polyt. Journ.*, cxlii. p. 365.

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THE CHEMICAL GAZETTE.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Boron. *By* MM. Wöhler *and* Sainte-Claire Deville.

Most of the simple bodies, at least those which have been more completely examined, present themselves under interesting forms. Boron alone, placed between carbon and silicium, both of which crystallize most perfectly, formed an exception to this rule. Investigations upon this substance, commenced by the authors separately but completed in common, have put an end to this exception, by showing that boron exists in three distinct states, thus presenting the same analogies as silicium to carbon, but in a still more marked degree*.

1. *Crystallized Boron, or Diamond of Boron.*—This substance was obtained in the form of transparent crystals, sometimes of a garnet-red and sometimes of a honey-yellow colour, although the colour could not be regarded as specific, for, like that of precious stones, it might be due to exceedingly small and variable quantities of foreign matters, especially silicium, carbon, or even amorphous boron. It is therefore to be hoped that crystallized boron may be obtained colourless.

The crystals possess such brilliancy and refractive power as to be only comparable to the diamond. This extreme refractive power is the cause of the metallic aspect of crystals of too large a size to be traversed by light. Probably, if boron should be obtained in large colourless crystals, it would present exactly the aspect of the diamond.

Another very important analogy is its hardness. Boron scratches corundum with the greatest ease, so that a cut sapphire, submitted to the action of the powder of boron, very rapidly lost its angles. A cut diamond, with which the crystals of boron were crushed upon a surface of polished quartz, was slightly attacked at all the points of contact. Boron must therefore be regarded as the hardest of all known bodies, or at all events next to the diamond.

The crystalline form of boron has still to be ascertained. The authors have frequently obtained pretty large crystals of boron; but on closely examining these, they proved to be very complicated macles, produced by the regular aggregation of a great number of very

* The boron analogous to ordinary carbon was discovered by Gay-Lussac and Thenard, by the reaction of potassium upon boracic acid.

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small elementary crystals. From their behaviour towards polarized light, the crystals do not appear to belong to the regular system.

Pulverulent boron, which it is almost impossible to obtain pure by the process of Berzelius, was fused by M. Despretz with the pile. With the heat of the oxyhydrogen flame, no perceptible fusion took place with crystallized boron. Crystallized boron, when strongly heated, resists the action of oxygen; it becomes oxidized at the temperature at which the diamond burns, but a little stratum of boracic acid, which forms upon its surface and is easily seen, prevents the extension of the action.

Chlorine, on the contrary, acts with remarkable energy upon boron, which becomes red-hot in an atmosphere of this gas, and is converted into gaseous chloride of boron; it is difficult to get chlorine sufficiently dry to avoid the production of a little vapour in this experiment, and a little boracic acid is deposited, arising from the water and air contained in the chlorine. Crystallized boron burns without residue; the apparent inflation of the crystals, characteristic of the combustion of the diamond in oxygen, is also manifested.

When heated with the blowpipe between two plates of platinum, it immediately causes the fusion of the metal in consequence of the formation of a boride*. No acids, whether pure or mixed, have any action upon boron, either cold or hot; at a red heat bisulphate of potash converts it into boracic acid, with evolution of sulphurous acid.

Boiling concentrated caustic soda does not change it; but monohydrated soda and carbonate of soda dissolve it slowly at a red heat. Nitrate of potash does not appear to act upon crystallized boron at this temperature; it is therefore the most unalterable of all simple bodies.

It is prepared by fusing together in a charcoal crucible 80 grms. of aluminium in large fragments, and 100 grms. of fragments of fused boracic acid. The charcoal crucible is luted into a good black-lead crucible, and the whole put into a blast-furnace capable of easily fusing pure nickel. The temperature is kept at its maximum for about five hours, care being taken to clear the bars of all ashes. When cold, the crucible is broken, and two distinct strata are found in it,—one vitreous, composed of boracic acid and alumina, and the other metallic and cavernous, of an iron-gray colour, beset with little crystals of boron; it is aluminium, impregnated throughout with crystallized boron. All the metallic portion is treated with a moderately concentrated boiling solution of soda, which dissolves the aluminium; then with boiling muriatic acid, which removes the iron; and lastly, with a mixture of hydrofluoric and nitric acids, to extract the traces of silicium, which the soda may have left mixed with the boron. The boron is not pure, however; it contains laminæ of aluminium, which may be extracted mechanically, but cannot be separated from the boron by any chemical process.

The vitreous matter, when boiled with water, gives a large quan-

* Very curious alloys of boron with platinum and palladium have been obtained.

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tity of boracic acid and a gelatinous matter, which is nearly pure alumina. The spontaneous separation of alumina from boracic acid is in accordance with Rose's observations on the action of water upon the borates with insoluble bases.

2. *Graphitoid Boron.*—Aluminium dissolves but little boron. Thus it is usually obtained only in small quantity in this new form, when an alloy of boron and aluminium is dissolved in the way already described for the preparation of graphitoid silicium. A little is obtained in the preceding experiment, and it is easily separated from the crystallized boron from the facility with which it may be suspended in water. Graphitoid boron may also be easily produced by treating fluoborate of potash with aluminium, and adding as a flux a mixture of equal equivalents of the chlorides of potassium and sodium. Small ingots of boride of aluminium are obtained, and these, when dissolved in muriatic acid, deposit the boron in its second modification. This consists of spangles, which are often hexagonal; they are slightly reddish, and have exactly the form and brilliancy of natural graphite and graphitoid silicium. It is completely opake.

3. *Amorphous Boron,* or *Boron of* Gay-Lussac *and* Thenard.—This is also produced in the experiment which yields crystallized boron; it is sufficient for this purpose that a small globule of aluminium should be in contact with a great mass of boracic acid. The reaction then takes place rapidly; the aluminium cannot dissolve the boron as fast as it is separated, and after the action of soda and acids a bright chocolate-brown substance is obtained, having all the properties assigned by Gay-Lussac, Thenard, and Berzelius to the amorphous boron with which they were acquainted.

When amorphous boron is collected on a filter, all that remains adhering to the latter when well dried, burns with remarkable facility and brilliancy when the paper is set on fire. Graphitoid boron, on the contrary, resists the heat produced by the combustion of paper.

From these facts it appears that boron should be placed still nearer than silicium to carbon.—*Comptes Rendus,* Dec. 8, 1856, p. 1088.

On the Preparation and Properties of Manganese.
By C. Brunner.

After indicating how he obtains pure sulphate from the native peroxide of manganese, and converts this into fluoride, the author states, that the reduction of the metal is effected exactly like that of aluminium. A Hessian crucible is half-filled with alternate layers of fluoride and sodium in thin plates of 1 to 2 millims—1 part of sodium to 2 parts of fluoride; the mixture is carefully pressed with a pestle, to leave as few interstices as possible, covered with a layer of dry chloride of sodium of about half the height of the mixture, and the whole is covered with a layer of fluoride of calcium, in fragments of the size of a pea. This serves to prevent the mixture from being projected from the crucible by the violence of the reaction.

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The crucible, thus charged and covered with its lid, is placed in a furnace communicating with the draught of a forge or a ventilator, and gently heated at first. Long before the incandescence of the crucible the reduction takes place. It is indicated by a hissing in the interior of the mass, and a yellow flame rising from the crucible. The heat is then increased and brought to whiteness. A quarter of an hour in all is sufficient. The apparatus is allowed to cool by stopping all the apertures of the furnace, and on breaking the crucible the reduced metal is found in a single ingot at the bottom.

The quantity of metal indicated by theory is not obtained. The composition of the fluoride is Mn Fl (Regnault); 100 parts of sodium should therefore decompose 203·5 parts of fluoride, forming 183·5 parts of fluoride of sodium and 120 parts of manganese. The process gives a little more than one-half of this. Sometimes the metal is not perfectly fused. In this case it is broken into small fragments in a steel mortar, and fused again, covered with chloride of sodium or potassium mixed with $\frac{1}{10}$th of nitrate of potash. The same plan is adopted to unite several small masses. Borax cannot be used as a flux, as it alters the metal considerably.

Manganese thus prepared possesses properties essentially different from those usually attributed to this metal. Its colour is like that of some cast iron; it is brittle and presents no resistance to the hammer or other mechanical forces; it is very hard, not yielding to a steel file, but, on the contrary, scratching the best tempered steel. It is capable of the most perfect polish. It is not altered even in moist air at the ordinary temperature. Polished fragments kept in the laboratory for two months lost none of their brightness. When heated upon platinum foil it acquires nearly the same colours as steel, passing afterwards to brown, by covering itself with a layer of oxide. The sp. gr. of different specimens varied from 7·138 to 7·206.

It is not attracted by the magnet, even when in powder, and has no influence on the magnetic needle. Acids attack it violently. In concentrated sulphuric acid in the cold it only causes a very slight evolution of gas, which appears to be merely hydrogen from the water contained in the acid. Heated with this acid it produces sulphurous acid and dissolves. Dilute sulphuric acid dissolves it readily in the cold.

Nitric acid dissolves it rapidly, as does also muriatic acid, even when diluted with much water, as well as acetic acid.

Manganese thus prepared will no doubt find applications in the arts. An acute-angled fragment may replace the diamond for cutting glass, and even for working in steel and other metals. It may be useful to engravers. The polish of which it is capable appears to render it applicable to optical purposes, such as the mirrors of telescopes. It cannot be forged, but may be cast as easily as iron. Its alloys may probably present useful properties.—*Comptes Rendus*, 23rd March, 1857, p. 630.

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Researches on the Ammonia-cobalt Bases.

By Wolcott Gibbs *and* F. A. Genth.

[Continued from page 148.]

Chloride of Roseocobalt.—An ammoniacal solution of chloride of cobalt absorbs oxygen readily from the air, becomes at first brown, and then gradually passes through various shades of colour to a deep red. The red solution leaves upon a filter a quantity of hydrate of sesquioxide of cobalt, which is sometimes almost inappreciable, sometimes in comparatively large amount. In one experiment, in which we employed perfectly pure chloride of cobalt and pure ammonia, there was no deposit whatever of oxide. In this case, however, no chloride of roseocobalt, but only chloride of purpureocobalt, was formed. When impure materials are used, the precipitate is abundant, and contains many of the impurities of the substances employed, as well as much sesquioxide of cobalt. The rate at which oxygen is absorbed varies much with the degree of concentration of the solution, with the temperature, with the quantity of ammonia present, and with the extent of liquid surface exposed to the air. Frequent agitation of the solution materially shortens the time required for complete oxidation, and the same effect is produced by passing a current of oxygen directly through the liquid, which soon becomes brown and subsequently red. As a general rule, the first effect of the oxidizing action is to give the liquid a brown colour, the layer next the surface being the first to change its tint. The brown colour then passes gradually into a deep red, and the oxidation is complete, when the whole mass of liquid has the colour of red Burgundy wine.

The presence of chloride of ammonium is not necessary in this process; a large quantity of this salt in the solution often gives a lilac or purple precipitate as the oxidation advances, but this is composed principally of the chloride of purpureocobalt. As will be seen from the above, the chloride of roseocobalt is not always formed during the oxidation of an ammoniacal solution of chloride of cobalt. On the contrary, it often happens that not a trace of this salt can be obtained from the oxidized solution, which contains only the chloride of purpureocobalt. We have observed the absence of the chloride of roseocobalt only in solutions which had been oxidized in a warm room or during the summer season. This fact, taken in connexion with the facility with which heat transforms solutions of roseocobalt into those of purpureocobalt, renders it, to say the least, extremely probable, either that a comparatively high temperature prevents the formation of the chloride of roseocobalt entirely, or else that this salt is converted into chloride of purpureocobalt as fast as it is formed in the solution.

To obtain the chloride of roseocobalt from the oxidized solution, cold and strong hydrochloric acid is to be added to it, the slightest elevation of temperature being carefully avoided. A brick-red precipitate is thrown down, which is to be washed with strong hydrochloric acid and then with ice-cold water, thrown upon a filter, and

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dried by pressure, great care being taken to operate at as low a temperature as possible.

As the formula of the chloride of roseocobalt is $5NH^3 . CO^2 Cl^3 + 2HO$, its formation by the oxidation of the ammoniacal solution of chloride of cobalt may be explained by the equation—

$$6CoCl + 10NH^3 + 3O = 2(5NH^3 . Co^2 Cl^3) + Co^2 O^3.$$

In those cases in which no sesquioxide of cobalt is precipitated, we may suppose that the sesquioxide unites directly with ammonia, as represented by the equation—

$$6CoCl + 15NH^3 + 3O = 2(5NH^3 . Co^2 Cl^3) + 5NH^3 . Co^2 O^3.$$

On adding an excess of hydrochloric acid to such an oxidized solution, $3(5NH^3 . Co^2 Cl^3)$ must be formed, which satisfactorily explains the precipitation of the brick-red chloride by the acid.

Fremy assigns to the brown substance, which is the first product of the oxidation, the formula $4NH^3 . Co^2 O^3$. We have not yet been able to obtain this substance in a condition fit for analysis, and Fremy does not consider the formula which he proposes as by any means established.

It will be seen from the above, that, in the formation of the chloride of roseocobalt, the elements of ammonia unite with sesquioxide or sesquichloride of cobalt at the instant that these are formed by the absorption of oxygen from the air. Claus has recently shown that the sesquichloride of rhodium* unites directly with 5 equivs. of ammonia to form a chloride exactly analogous to the chloride of roseocobalt, and having the formula $5NH^3 . Rh^2 Cl^3$. We have made various experiments to determine whether sesquioxide of cobalt once formed could unite directly with ammonia. A solution of chloride of ammonium was poured upon freshly-prepared sesquioxide of cobalt, strong ammonia-water added, and the whole allowed to stand for some time in a closed bottle and in a rather dark closet. Even after many weeks, however, only traces of chloride of roseocobalt could be detected. A quantity of sesquioxide of cobalt was dissolved in strong acetic acid, and to the solution chloride of ammonium and ammonia-water added. In this case chloride of roseocobalt was formed after a few days, but it is doubtful whether its formation was not due to the oxidation of a small quantity of protoxide of cobalt in the sesquioxide employed. In another experiment, strong ammonia was added to freshly-prepared sesquioxide of cobalt, and the whole allowed to stand for several weeks, after which time it was boiled with hydrochloric acid, and considerable quantities of chloride of purpureocobalt, luteocobalt, and praseocobalt were obtained. This experiment leaves no doubt that the ammonia-cobalt bases can be prepared by the direct action of ammonia upon sesquioxide of cobalt, though this mode of preparation is not œconomical.

The chloride of roseocobalt may also be prepared by adding cold and strong hydrochloric acid to a completely oxidized solution of the ammoniacal nitrate or sulphate of cobalt. A brick-red precipi-

* Since the above was written, Claus has extended his observation to the sesquichloride of iridium, which forms a similar base with 5 equivs. of ammonia.

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tate is formed in either case, which must be purified by repeated washing with hydrochloric acid. Strong hydrochloric acid also precipitates the chloride from solutions of the sulphate and nitrate of roseocobalt. In all these cases, however, it is difficult to obtain the chloride in a perfectly pure state.

The chloride of roseocobalt is usually precipitated as a brick-red powder, which under the microscope appears to be composed of indistinct granular crystals. It may be purified, though with difficulty, by solution in ice-cold water and spontaneous evaporation in the cold. The salt is soluble in cold, as well as in hot water, with a dark red but not a violet-red colour, the portions still undissolved becoming lilac or purple before dissolving. The most remarkable property of this salt is the facility with which it is converted into chloride of purpureocobalt. The hot solution yields on cooling small but brilliant crystals of the latter chloride; in fact, even solution in warm water converts a portion of chloride of roseocobalt into chloride of purpureocobalt, as may easily be observed by the change of colour. This transformation is, however, far more striking when a solution of chloride of roseocobalt is boiled with a little hydrochloric acid; the solution speedily changes its colour from a dull red to a beautiful violet-red, and on cooling deposits an abundant crystallization of chloride of purpureocobalt. There is in this case a direct conversion of roseocobalt into purpureocobalt, an isomeric radical; the reactions of the violet-red solution being entirely different from those of the same solution previous to boiling with acid, except in one or two particulars, to be pointed out hereafter. The dry chloride of roseocobalt is also slowly converted into chloride of purpureocobalt by keeping, changing its colour to violet-red; in this case, however, the change is not complete, even after a long time, unless heat be applied. The formula of the chloride of purpureocobalt, as we shall hereafter show, is

$$5NH^3 . Co^2 Cl^3.$$

This differs from that of the chloride of roseocobalt only by containing no water of crystallization. The change which takes place in the conversion of one chloride into the other does not, however, consist in the mere loss of water. As we shall show, the chloride of roseocobalt corresponds to a triacid oxide, while that of purpureocobalt yields a biacid oxide. It is to be carefully borne in mind, that the substance which we have called chloride of roseocobalt is not the chloride of roseo-cobaltiaque of Fremy, Claudet, and other chemists who have studied the subject. To the chloride described by Fremy under the name of chloride of roseocobaltiaque, we have given the name of chloride of purpureocobalt. The necessity of this change of name has arisen from the fact, that hitherto two different bases have been confounded, the chloride of purpureocobalt having been considered as the chloride corresponding to the sulphate and nitrate of roseocobalt.

The chloride of roseocobalt is dichrous, the ordinary being paler than the extraordinary image; both are rose-red, with a faint brownish-orange tint.

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Chloride of roseocobalt, as already mentioned, has the formula $5NH^3 . Co^2 Cl^3 + 2HO$, which requires—

	Calculated.	Found.	
Cobalt	21·97	21·99	22·10
Chlorine.....	39·66	39·57	39·71
Hydrogen	6·33	6·37	6·50
Nitrogen	26·08	26·16	

With respect to this formula, it must be remarked that it is extremely difficult to obtain this chloride perfectly free from chloride of purpureocobalt, into which it is so easily converted. The uncertainty, however, will concern only the number of equivalents of water. The chloride of roseocobalt combines with the chlorides of the electro-negative metals to form well-defined salts. The platinum-salt, which we have not yet fully examined, appears to have the formula—

$$5NH^3 . Co^2 Cl^3 + 3PtCl^2 + 8HO.$$

A neutral solution of the chloride of roseocobalt is easily decomposed by boiling, with evolution of ammonia, and precipitation of a black powder. This powder is probably a hydrate of the magnetic oxide $Co^3 O^4 + xHO$, but we have deferred its examination to the second part of our memoir. The reactions of the chloride of roseocobalt are as follows:—

Terchloride of gold gives no precipitate at first, but after standing a lilac or purple precipitate, which is probably merely the chloride of roseocobalt. Bichloride of platinum gives a pale orange-red precipitate. Chloride of mercury gives a pale rose- or flesh-coloured flocky precipitate. Ferridcyanide of potassium gives beautiful, orange-red, oblique, rhombic crystals. Cobalticyanide of potassium gives fine red crystals. Ferrocyanide of potassium gives a cinnamon-, passing to a chocolate-brown precipitate. Oxalate of ammonia gives a brick-red precipitate of small granular crystals. Neutral chromate of potash gives no precipitate. Bichromate of potash gives a dark brick-red precipitate. The following reactions, which were obtained with a solution of the hydrated nitrate of roseocobalt, may also be introduced in this place. Pyrophosphate of soda gives a dull rose-red precipitate, soluble in an excess of the precipitant to a clear red liquid, which in a few minutes solidifies to a mass of fine rose-red needles. Picrate of ammonia gives a fine bright orange-red precipitate, soluble in hot water. Iodide of potassium gives no precipitate either with the chloride or nitrate. The precipitate with chloride of mercury is readily soluble in hydrochloric acid, and the solution after standing gives beautiful small granular crystals of a brownish-red colour.

The reactions which are peculiar to the sulphate of roseocobalt will be described when speaking of that salt.

Sulphate of Roseocobalt.—An ammoniacal solution of sulphate of cobalt absorbs oxygen readily from the air, becoming at first brown and then dark red. The time required for complete oxidation varies

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remarkably. The process is sometimes complete in a few days, but often requires many weeks. From the perfectly oxidized solution, sulphuric acid cautiously added usually throws down the sulphate of roseocobalt as a bright red crystalline powder, which, after washing with cold water, is readily purified by solution and crystallization, a very small quantity of acid being added to prevent decomposition.

The sulphate of roseocobalt is, however, not always the only salt formed under these circumstances. In some cases in which the ammoniacal liquid was allowed to stand several months until there remained only a dry mass of red crystals, warm water dissolved out a red salt in small quantity, much more soluble than the sulphate of roseocobalt, and giving different and very characteristic reactions. In other cases, and especially when a little chloride of cobalt was originally present, warm water dissolved out another sulphate, crystallizing in octahedra of an orange-red colour, the examination of which is not yet complete.

We are unable to confirm Fremy's assertion, that sulphuric acid precipitates from oxidized ammoniacal solutions of sulphate of cobalt, an *acid* sulphate of roseocobalt, having the formula—

$$5NH^3 . Co^2 O^3, 5SO^3 + 5HO.$$

The salt precipitated under these circumstances is merely the neutral sulphate, as repeated analyses have shown, and as the crystalline form at once proves. The formula of the neutral sulphate is $5NH^3 . Co^2 O^3, 3SO^3 + 5HO$, which requires—

	Equivs.	Calculated.		Found.	
Cobalt	2	59·0	17·71	17·72	17·79
Sulphuric acid	3	120·0	36·03	36·11	36·38
Hydrogen.....	20	20·0	6·00	6·14	6·15
Nitrogen	5	70·0	21·02	20·95	20·08
Oxygen.....	8	64·0	19·24		

The sulphate of roseocobalt has a fine cherry-red colour. The light reflected from a layer of the crystals, when analysed by the dichroscopic lens, gives a rose-red ordinary, and an orange-red extraordinary image. The dichroism is very distinct. In this, as in our other observations upon dichroism, the reflected rays examined made an angle of about 60° with the normal, but no material variations of colour could be observed by changing the angle of incidence. The exact colour of the crystals is, according to Chevreul, the second red $\frac{2}{10}$ths. The crystals of sulphate of roseocobalt belong to the dimetric or square prismatic system.

The sulphate of roseocobalt is nearly insoluble in cold water, but is soluble in much boiling water, and crystallizes readily as the solution cools. By slow evaporation, it may be obtained in large crystals, which however seldom exhibit very perfect faces. Ammonia in dilute solution dissolves the sulphate, giving a fine purple solution, from which the salt crystallizes unchanged. The neutral solution is readily decomposed by boiling, ammonia being evolved, and a dark brown precipitate of the hydrated magnetic oxide of cobalt,

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$Co^3 O^4 + 3HO$, thrown down, while sulphate of luteocobalt remains in solution. The decomposition in this case extends to the sulphate of luteocobalt also, so that much less than 1 equiv. of this salt is obtained for 2 equivs. of the sulphate of roseocobalt decomposed.

Strong ammonia poured upon dry sulphate of roseocobalt, usually changes its colour almost immediately from a red to a buff-yellow, while the liquid itself becomes red. The buff-coloured substance formed in this case is the sulphate of luteocobalt; the red solution contains sulphate of roseocobalt.

When dry sulphate of roseocobalt is carefully heated in a porcelain or platinum crucible, ammonia is evolved, and there remains a lilac-red mass, which contains sulphate of luteocobalt, sulphate of purpureocobalt, and a leek-green crystalline substance, which we have called provisionally Praseocobalt.

We shall speak of all these reactions more fully when treating of the sulphate of luteocobalt.

A current of the red gas which arises from the action of nitric acid upon starch, and which probably consists chiefly of NO^4, converts an acid, neutral, or ammoniacal solution of sulphate of roseocobalt into one of the nitrate of xanthocobalt.

A solution of sulphurous acid gently heated with sulphate of roseocobalt gives, in a few minutes, an orange precipitate of a substance containing ammonia, sesquioxide of cobalt, sulphurous and sulphuric acid, and which we shall describe fully in the second part of our memoir.

Strong sulphuric acid digested with sulphate of roseocobalt yields, under some circumstances, sulphate of ammonia and sulphate of luteocobalt. In other cases it yields the acid sulphate of purpureocobalt. By double decomposition with salts of barium, the sulphate of roseocobalt yields the other salts of this base.

The reactions of the sulphate are somewhat different from those of the chloride, as will be seen from the following statement:—

Ferridcyanide of potassium gives no precipitate at first, but after two hours very distinct and well-defined, small, augitic crystals. Cobalticyanide of potassium behaves in a precisely similar manner, giving red crystals. Neutral chromate of potash gives no precipitate. The bichromate gives none at first, but after two or three hours groups of reddish-brown needles.

We shall hereafter state our reasons for believing that in certain cases there is a conversion of the triacid roseocobalt in the sulphate of this base, into the biacid purpureocobalt.

Anhydrous Nitrate of Roseocobalt.—The ammoniacal solution of nitrate of cobalt absorbs oxygen very readily from the air, and the oxidation is usually complete after a few days. As a general rule, a considerable quantity of nitrate of luteocobalt is formed under these circumstances, and being insoluble in the ammoniacal liquid, forms a bright yellow crystalline precipitate upon the bottom and sides of the vessel. During the process of the oxidation, crystals of the compound described by Fremy as the nitrate of oxycobaltiaque are frequently formed in some quantity; but these disappear at a

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later stage of the oxidation, when the liquid takes a deep wine-red colour. The crystals of nitrate of oxycobaltiaque were first observed by Leopold Gmelin. We have not particularly examined or analysed them, though Fremy's analyses do not appear to us satisfactory.

The dark red liquid formed under these circumstances contains nitrate of roseocobalt. When nitric acid is added to this solution, a brick-red precipitate is thrown down, which is the hydrated nitrate of roseocobalt. This nitrate is readily soluble in water, and exists unchanged in the solution, but by boiling with nitric acid the solution yields a fine, violet-red, crystalline precipitate of the anhydrous nitrate of roseocobalt. The presence of nitrate of ammonia facilitates the oxidation and formation of nitrate of roseocobalt, but is not indispensable.

The preparation of pure nitrate of roseocobalt is attended with difficulty, as the precipitated crystalline nitrate almost always contains a little nitrate of luteocobalt. It is best to dissolve the crude nitrate in water to which a little ammonia has been added, to filter, and allow the solution to evaporate spontaneously. After some days, large and well-defined crystals of the nitrate are formed, while the bottom of the evaporating vessel is covered with minute red crystals of the same salt. The difference between the appearance of the large and small crystals is so great, that we suspected a difference in their constitution. Analysis, and the behaviour of the two kinds towards reagents, showed, however, no difference. A marked variation in the colour of the large and small crystals of the same substance is very commonly observed in the ammonia-cobalt compounds, and might easily lead to erroneous conclusions. The nitrate of roseocobalt is readily prepared by decomposing a solution of the chloride with nitrate of silver, but the solubility of the chloride of silver in chloride of roseocobalt renders it somewhat difficult to obtain a pure salt in this manner. Nitrate of copper also gives nitrate of roseocobalt with chloride of copper, when mixed with an equivalent proportion of chloride of roseocobalt, but the purification is difficult. Finally, a pure nitrate may be prepared by double decomposition of nitrate of baryta and sulphate of roseocobalt. The anhydrous nitrate of roseocobalt, when in large crystals, has a fine red colour, which, according to Chevreul's determination, as given by Fremy, is the first red $\frac{2}{10}$. The crystals are dichrous; the ordinary image is clear rose-red, the extraordinary image bright red. According to Prof. Dana, this salt, like the sulphate, crystallizes in forms belonging to the dimetric system.

Ammonia dissolves the nitrate with a fine purple-red tint, and the salt usually crystallizes unchanged from the solution, though sometimes the hydrous nitrate is obtained. In cold water the nitrate is rather insoluble, though more soluble than the sulphate. Hot water dissolves it rather more easily; but the solution, unless it be acid, is quickly decomposed, and this effect is very speedily produced by boiling. The products of the decomposition in this case are a dark brown oxide of cobalt, and a solution containing the nitrate of luteocobalt and nitrate of ammonia. The quantity of luteo-

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cobalt is small in comparison with that of the nitrate of roseocobalt employed.

When heated, the nitrate of roseocobalt explodes, though not with violence. A black anhydrous oxide remains, which is probably $Co^2 O^3$. The reaction in this case is easily explained, if we remark that the oxygen in the nitric acid is exactly sufficient to form water with the hydrogen of the ammonia. The simplest equation representing the reaction is—

$$5NH^3 . Co^2 O^3, 3NO^5 = Co^2 O^3 + 8N + 15HO.$$

In point of fact, however, the decomposition is less simple, as red vapours are always evolved.

When a current of NO^4 is passed through a solution of nitrate of roseocobalt, a rapid absorption takes place, and after a short time crystals of nitrate of xanthocobalt are deposited.

A solution of sulphurous acid converts the nitrate of roseocobalt at first into an orange-coloured compound containing SO^2, and afterwards reduces this completely to nitrate and sulphate of cobalt and nitrate of ammonia.

Nitrate of roseocobalt has the formula $5NH^3 . Co^2 O^3, 3NO^5$, which requires—

	Equivs.	Calculated.		Found.		
Cobalt	2	59·0	17·87	17·82	17·92	17·90
Hydrogen ..	15	15·0	4·55	4·64	4·79	4·57
Nitrogen ..	8	112·0	33·93	33·98	34·03	
Oxygen	18	144·0	43·65			

When nitrate of roseocobalt is dissolved in water containing much nitrate of ammonia and a little ammonia, and the solution is allowed to evaporate spontaneously, beautiful purple-red scaly crystals separate. These crystals cannot be purified by recrystallization, as they are decomposed by solution in water. When boiled with hydrochloric acid, there is copious effervescence, and a purple-red solution is obtained, which appears to contain the chloride of purpureocobalt. The empirical formula of the scaly nitrate appears to be $5NH^3 . Co^2 O^3, 2NO^5 + 7HO$. From the effervescence with muriatic acid we are disposed to consider it $4NH^3 . Co^2 O^3, NO^5 + NH^4 O, NO^5, +6HO$; but further investigation is required before we can pronounce with certainty on this point.

Hydrous Nitrate of Roseocobalt.—When ammonia is added in excess to a solution of the nitrates of cobalt and of ammonia, and the solution is exposed to the air, oxidation takes place with considerable rapidity, and as we have already stated when speaking of the anhydrous nitrate, the solution becomes dark purple-red, while yellow scales of the nitrate of luteocobalt are more or less abundantly deposited upon the bottom of the vessel. When the red liquid is boiled with nitric acid in excess, a dark crimson precipitate of nitrate of roseocobalt is formed, while a portion of the same salt remains in solution. It has hitherto been supposed from these facts, that the anhydrous nitrate of roseocobalt is a direct product of the

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oxidation of the ammoniacal liquid. This, however, is not the case. If the oxidized liquid be filtered from the nitrate of luteocobalt and allowed to evaporate spontaneously, very fine, large, oblique rhombic crystals are formed, which are the hydrous nitrate of roseocobalt.

The crystals of this nitrate belong to the monoclinic or oblique rhombic system, according to Prof. Dana's determination.

The hydrous nitrate of roseocobalt is readily soluble even in cold water; the hot neutral solution is very easily decomposed, with evolution of ammonia and precipitation of a black powder. The addition of a few drops of nitric acid prevents the decomposition. An excess of nitric acid added to a cold solution of the nitrate produces a brick-red precipitate, which is readily soluble in cold water, and which is the unchanged salt. The solution has a dark brick-red colour, and exhibits all the reactions of the chloride of roseocobalt. When boiled with an excess of nitric acid for some time, the brick-red colour gradually becomes violet-red, and there remains at last a beautiful violet precipitate, which is the anhydrous nitrate of roseocobalt. From this it appears that, in some cases at least, and particularly when nitrate of ammonia is present during the oxidation, the hydrous nitrate of roseocobalt is the first product of the oxidation of an ammoniacal solution of nitrate of cobalt, and that it is the action of nitric acid upon this salt which converts it into the anhydrous nitrate. The nitrate of roseocobalt obtained by direct oxidation may be recrystallized by adding to its solution a few drops of nitric acid, and allowing it to stand a few days for spontaneous evaporation. In this manner beautiful crystals are obtained, adhering to the bottom of the evaporating vessel, and mixed with a dull red matter in crystalline crusts, which exhibits the same reactions with the large and clear crystals, and appears to have the same constitution, though upon this point we cannot speak with certainty at present.

We consider the formula of the hydrous nitrate of roseocobalt as most probably $5NH^3 . Co^2 O^3, 3NO^5 + 2HO$, which requires—

	Equivs.	Calculated.	Found.	
Cobalt	2	16·95	17·05	17·09
Nitrogen	8	32·18	32·30	31·92

It is true that the analyses here agree with the formula as well as can be reasonably expected. We have, however, found in other crystals from the same mass 17·82, 17·86, 17·92, 18·06 per cent. cobalt, numbers which agree much better with the formula of an anhydrous nitrate, having the same formula as the nitrate of roseocobalt already described, which contains 17·87 per cent. In any event, the doubt appears to be simply with respect to the quantity of water in the salt, the ratio of the equivalents of cobalt and nitrogen being as 1 to 4, or 2 to 8. We shall return to this point at another time.

Oxalate of Roseocobalt.—The oxalate is precipitated from the chloride almost immediately by the addition of a solution of oxalate of ammonia. From a solution of the nitrate it is deposited much

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more slowly, often only after some hours, and sometimes in remarkably distinct and well-formed crystals. The oxalate, as first thrown down, may be purified by solution in ammonia-water and recrystallization by spontaneous evaporation. The salt then forms beautiful prismatic crystals, which are nearly insoluble in water, and which have a fine cherry-red colour, resembling the crystals of sulphate of roseccobalt. The crystals are dichrous, the ordinary image being pale violet, while the extraordinary image is dark rose-red. The precipitated oxalate has a dull brick-red colour. According to Prof. Dana, the crystals of oxalate of roseocobalt belong to the right rhombic or trimetric system, the observed forms being a rhombic prism of about 101° 48′, with a brachydome of 108° 54′.

The constitution of the oxalate of roseocobalt is represented by the formula $5NH^3 . Co^2 O^3, 3C^2 O^3 + 6HO$, which requires—

	Equivs.	Calculated.	Found.	
Cobalt	2	17·87	18·15	18·14
Oxalic acid	3	32·73	32·82	

Cobalticyanide of Roseocobalt.—This beautiful salt is precipitated from a solution of the chloride or hydrous nitrate of roseocobalt by a solution of cobalticyanide of potassium. It may be prepared with equal facility from a solution of the chloride of purpureocobalt, which under these circumstances, as we conceive, undergoes a direct change into a salt of the triacid roseocobalt. The cobalticyanide is usually precipitated at once in the form of cherry-red prismatic crystals, which, so far as it is possible to judge from their appearance under the miscroscope, belong to the oblique rhombic or monoclinic system, much resembling some of the simpler forms of augite. The salt is very insoluble in cold water; hot water readily decomposes it. It forms an extremely characteristic test for the salts of roseocobalt in general, as well as for the chloride of purpureocobalt, but, as already remarked, it is precipitated from the sulphate of roseocobalt only after some hours. The crystals are usually remarkably large when compared with the mass of liquid from which they are thrown down. They are more distinct in form the more slowly the precipitation takes place. The salt has the formula $5NH^3 . Co^2 Cy^3 + Co^2 Cy^3 + 3HO$, which requires—

	Equivs.	Calculated.	Found.	
Cobalt	4	30·57	30·63	30·46
Nitrogen	11	39·89	40·18	

The analyses of the ferridcyanide of roseocobalt give additional evidence of the correctness of the formula adopted for this salt.

Ferridcyanide of Roseocobalt.—The ferridcyanide is formed like the cobalticyanide by adding a solution of ferridcyanide of potassium to one of chloride or nitrate of roseocobalt or chloride of purpureocobalt. A very beautiful orange-red precipitate is thrown down in distinct and usually extremely well-defined crystals, which under the microscope exactly resemble those of the corresponding cobalt-salt. The crystals exhibit a remarkable dichroism, the ordi-

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nary image being of a fine purple-rose colour, while the extraordinary image is bright orange-red. The crystals are insoluble in cold water; hot water easily decomposes them, ammonia being evolved, while a dark brown precipitate is thrown down. Heat decomposes the dry salt very gradually and uniformly, and leaves a black residue, which contains much carbon. We availed ourselves of this fact to determine accurately the sum of the cobalt and iron in the salt, by first decomposing it by heat, then burning off the carbon in a gentle current of oxygen, and finally reducing the mixed oxides of cobalt and iron in a current of hydrogen. The formula of this salt is $5NH^3 . Co^2 Cy^3 + Fe^2 Cy^3 + 3HO$, which requires—

	Equivs.	Calculated.	Found.
Cobalt and iron	4	30·02	30·05
Carbon	12	18·79	18·69

There can be no reasonable doubt that this salt is isomorphous with the corresponding cobalt-salt. Like the latter, it is an extremely valuable test for the salts of roseocobalt and for certain salts of purpureocobalt.

Oxide of Roseocobalt.—The oxide of roseocobalt exists only in solution. It is obtained either by decomposing the chloride by oxide of silver, or by adding baryta-water to a cold solution of the sulphate; the latter method is the better one, because the chloride of silver is soluble in solutions of the chloride of roseocobalt. The solution as thus obtained is red, has an alkaline non-metallic taste and reaction, and is very easily decomposed. By standing in the air, it absorbs carbonic acid, and forms a carbonate.

Magnetic Oxide of Cobalt.—In connexion with the salts of roseocobalt, we may perhaps with propriety describe the peculiar oxide of cobalt, which is, in some cases at least, one of the products of their decomposition. The hydrated oxide which is precipitated by boiling the neutral salts of roseocobalt with an alkaline solution, is considered by Fremy as a hydrate of the sesquioxide, and he attributes to it the formula $Co^2 O^3, HO$. According to the same chemist, all the other ammonia-cobalt bases give this hydrate by boiling with solutions of the alkalies. It does not appear probable that the oxide obtained by boiling the neutral solution should have a different constitution. We have, however, found that the dark brown oxide obtained by boiling a solution of sulphate of roseocobalt, and afterwards washing and drying the precipitate in the air, has the formula $Co^3 O^4 + 3HO$, which requires—

	Equivs.		Calculated.	Found.
Cobalt	3	88·5	60·00	60·05
Oxygen	4	32·0	21·69	21·38
Water.....	3	27·0	18·30	18·03

Fremy's formula requires 64 per cent. of cobalt. Claudet gives also the formula $Co^3 O^4 + 3HO$ as probable, but without analyses. On the other hand, it is possible that the different salts, not only of roseocobalt but of the other similar bases, may give different oxides by decomposition. We propose to examine this point more fully hereafter.

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The hydrate above mentioned and analysed is a very dark brown powder, which dries to a black mass with a gummy lustre. The powder is dark brown. Oxalic acid dissolves it to a green solution, without evolution of gas, but this is decomposed by heating. Hydrochloric acid also dissolves the oxide, with evolution of chlorine and formation of the protochloride.

We have already mentioned, that the anhydrous magnetic oxide of cobalt is sometimes obtained during the decomposition of the chloride of roseocobalt by heat. We are, however, not able to state precisely under what circumstances this occurs; either water or the oxygen of the air must take part in the decomposition, since the chloride contains no oxygen. The anhydrous oxide occurs in the form of small steel-gray octahedra, which are very hard, and which can only be dissolved by long heating with sulphuric acid, or by fusion with sulphate of potash. Nitric, hydrochloric, and nitro-muriatic acids have no decided action upon them.

1·6425 gr. of this oxide gave 1·2059 gr. of metallic cobalt =73·41 per cent.

1·6425 gr. ignited in hydrogen gave 0·4879 gr. water=25·91 per cent. oxygen.

The formula $Co^3 O^4$ requires—

	Equivs.		Calculated.	Found.
Cobalt	3	88·5	73·44	73·41
Oxygen	4	32·0	26·56	25·01

This oxide has recently been described by Schwarzenberg, who obtained it by igniting chloride of cobalt with free access of air, until the chlorine is expelled. It is therefore very probable that in the decomposition of chloride of roseocobalt by heat, the chloride of cobalt is first produced, and then decomposed in the manner observed by Schwarzenberg.

With respect to the black sulphide which is thrown down from solutions of the ammonia-cobalt bases by sulphide of ammonium, it can scarcely be doubted that this is the bisulphide, as Claudet's analyses lead directly to the formula CoS^2, corroborating the results obtained by Dingler already alluded to.

[To be continued.]

Note on Crystallized Chromium and its Alloys. *By* E. Fremy.

The object of the author's investigations was the comparative examination of iron, manganese, and chromium, which form a true chemical family, and the determination of the influences which may cause the properties of these metals and their alloys to vary according to the mode of preparation. He ascertained that manganese and chromium were obtained in a state of absolute purity by Wöhler's process, by submitting their anhydrous chlorides to vapour of sodium. The decomposition is effected in a porcelain tube heated to redness; the metallic chlorides are placed in little trays, and the vapour of sodium is carried in by a current of hydrogen. Under

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the influence of the alkaline chloride produced, and perhaps also by the action of the current of gas, the reduced metals affect regular crystalline forms.

Chromium forms crystals which possess great brilliancy when freed from the alkaline chloride; the crystals belong to the cubic system. They are very hard, and possess the curious property of resisting the action of the most energetic acids, and even nitro-muriatic acid.

These facts, resembling those recently ascertained by Deville regarding aluminium, show that many elements are still wanting to establish a natural classification of metals.

The alloys of chromium with other metals often possess the hardness of chromium, and like it resist the action of concentrated acids. The alloy of chromium and iron was obtained either by reducing chromate of iron with charcoal, or by heating iron and pure oxide of chromium in the forge. This alloy crystallizes sometimes in long needles; it resembles brass, and scratches the hardest bodies.

The green sesquioxide of chromium may be easily fused at the heat of a forge, when it is converted into a black crystalline mass, which presents all the characters of the crystallized sesquioxide of chromium obtained by Wöhler by decomposing chlorochromic acid by heat. This fused oxide may be obtained in considerable quantity; it readily scratches quartz and tempered steel; and, as well as the alloys of chromium, it may find some applications in the arts.—*Comptes Rendus*, March 23, 1857, p. 632.

On the Properties of some Salts of Uranium.
By R. Arendt *and* W. Knop.

In the further elaboration of the determination of phosphoric acid by salts of uranium, we were compelled to investigate more closely the properties of some compounds of uranium, as hitherto but little has been done with these salts.

The material from which we start in the preparation of uranium compounds will probably always be pitch-blende; and since Patera has done such service in the working of this, it is to be expected that crude material containing oxide of uranium will in future be more accessible than is the case at present. With a view to the employment of uranium as a reagent, it would be of the greatest use to employ a method in which fixed alkali would be avoided, or at least got rid of again immediately in the manufacture on the large scale; carbonate of uranium and ammonia is the most advisable compound from which to proceed in the preparation of other salts.

The alkali can only be got rid of from carbonate of uranium and potash or soda, by dissolving it at least three times in muriatic acid and precipitating by ammonia, in which the best plan to adopt is to put the precipitate upon bibulous paper as soon as the mother-liquor has been filtered away, dry it in the drying chamber, and then triturate and wash it; otherwise its considerable volume does not allow it to be completely washed.

All oxide of uranium which has been prepared on the large scale

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from pitch-blende contains iron. For the separation of this carbonate of ammonia is employed; this dissolves the oxide of uranium, but leaves the iron undissolved. This mode of separation has even been employed in quantitative analysis, but it has already been stated by H. Rose, that it may easily prove unsuccessful.

For the separation of iron from uranium we have adopted a different process, founded upon the behaviour of oxide of uranium to ammoniacal salts.

Thus if from a fluid containing much muriate or acetate of ammonia we precipitate some oxide of uranium by means of ammonia, and then boil it for some time, the oxide of uranium expels ammonia, and dissolves again completely. When therefore we have oxide of uranium containing iron in a solution, and add ammonia to this until all the uranium and iron is precipitated, dissolve the precipitate in acetic acid, then again add carbonate of ammonia until precipitation just commences, and then boil it long enough, the iron is thrown down. The solution of uranium thus produced is perfectly free from iron. If alumina be present, this is also precipitated with the iron.

The same process also gave us the best results in quantitative operations, only that in this case the iron precipitate must be subsequently extracted with a little carbonate of ammonia without the application of heat, as the iron deposited contains a small proportion of uranium. The separation of iron from uranium by means of acetate of ammonia is therefore of such a nature, that in the first operation the uranium is obtained in the solution free from iron; but, on the contrary, the iron is not free from uranium, and this can only be attained by a second operation.

From a solution of uranium, which has first been neutralized, then mixed with succinate of ammonia, and lastly with an excess of carbonate of ammonia, the greater part of the iron is thrown down as succinate of iron, whilst the succinate of uranium remains in solution. At the same time, however, a large quantity of iron remains in solution, which separates with a portion of uranium when the ammoniacal solution is evaporated. On the one hand the iron remains in solution with the uranium, and on the other uranium with the iron, so that no good separation is effected in this way.

Perchloride of Uranium, obtained by dissolving carbonate of uranium and ammonia, or the precipitate obtained by precipitation with caustic ammonia in muriatic acid, is reduced to protochloride by sulphuretted hydrogen with very great difficulty, and the reduction is probably scarcely complete. Zinc reduces it rapidly, as do iron and tin when they are converted into the positive pole of a galvanic element, which is easily done by the addition of a few drops of perchloride of platinum.

The reduction takes place immediately by means of tin in a very strong solution in muriatic acid; but the dissolved tin is very difficult to get rid of again from the solution, because the monosulphuret of tin is too easily soluble in the quantity of muriatic acid which is set free by the sulphuretted hydrogen employed. If the action of

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the acid were to be avoided by a very considerable dilution with water, there would be danger of precipitating uranium in the form of sulphuret. None of the above-described methods therefore is adapted to the preparation of protochloride and protosalts of uranium.

The method by which Peligot first obtained protochloride of uranium in the beautiful form of green crystals, is too circumstantial when it is to be frequently prepared. We have therefore devised a new method for obtaining protochloride of uranium conveniently and quickly in any desired quantity, and from this the other protosalts may be prepared. The process is as follows:—

Quantities of about ½ lb. of carbonate of uranium and ammonia are dissolved in twice as much muriatic acid as is necessary for their solution alone; the acid may be diluted with an equal volume of water. From 4 to 6 drops of a strong solution of perchloride of platinum are added thereto, and an excess of fine copper turnings are thrown into the mixture. It is then heated, and allowed to boil for scarcely a quarter of an hour. The fluid very rapidly acquires a deep green colour, and the perchloride is very soon converted into protochloride.

In this process our object was to obtain an agent which,—1st, indicates the completion of the reaction immediately; and 2ndly, allows of the deposition of the reducing body. The protochloride of copper which is produced in this case satisfies both these requirements, as it is very difficult of solution in water.

The green fluid is therefore allowed to boil until a few drops of it, poured into water, fill the latter immediately with the white crystalline powder of protochloride of copper. The green solution itself is then diluted, and allowed to become perfectly cold, by which means the protochloride of copper separates within a very small quantity, and sulphuretted hydrogen is passed into the filtered solution until all the copper is precipitated, and the fluid smells permanently of sulphuretted hydrogen. Thus we have only to precipitate the quantity of copper which remains in the form of protochloride dissolved in the fluid; whilst with other metals, for example when tin has been employed in the reduction, the entire quantity of the metal dissolved by the muriatic acid must be precipitated.

In this state it is poured into a porcelain dish, and boiled with a brisk fire. At first some protoxide and sulphuret of uranium are sometimes deposited, but these generally dissolve again towards the end. Solutions containing much muriate of ammonia do not so readily let fall this precipitate, which moreover may be dissolved by a little concentrated muriatic acid when it has fixed itself on the dish. The sulphuretted hydrogen is driven off with great difficulty; a solution prepared from the above-mentioned quantity of peroxide of uranium must be boiled down to about 400 cub. centims. before the sulphuretted hydrogen is driven off, and if the solution of the protochloride is to be employed directly, much muriate of ammonia must be added to it.

Properties of the Solution of Protochloride of Uranium.—The solution thus prepared contains muriate of ammonia, which is no

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hindrance to the preparation of the salts, as, if necessary, the protoxide may be precipitated from the solution by ammonia, and again dissolved. If it be dropped into water previously brought to a full boiling heat, black protoxide of uranium is thrown down, and the acid passes freely into solution. The decomposition is perfectly complete, and the water above the precipitate quite colourless. This behaviour may perhaps be employed in the separation of uranium from many other metals.

Solution of protochloride of uranium is an excellent reducing agent, and deserves to be employed as such in analysis. When it is free from iron, it remains unchanged in the air; at least we have observed no change of the green colour into the yellow of the perchloride in the course of one to two months, in bottles the bottom of which was scarcely covered with the solution. If the uranium contain iron, this becomes oxidized, and is again reduced by the protochloride of uranium until both are converted into perchloride. In solutions of peroxide of iron this is reduced to protoxide by protochloride of uranium, even at ordinary temperatures. At a boiling heat this reduction is instantaneous.

If it be desired, for any analytical purpose, to reduce peroxide of iron in solution to protoxide, we have in protochloride of uranium the best agent with which we are acquainted, for the completion of the reaction is immediately recognizable by the disappearance of the red colour of the iron solution, which is replaced by green as an excess of protochloride of uranium is formed. Moreover, this reaction may also be rendered very distinctly recognizable by other means. If a drop of solution of sulphocyanide of potassium be added to the iron solution, the deep red colour thus produced persists until the drop of solution of protochloride of uranium which reduces the last traces of peroxide of iron is added, and, on the other hand, the red colour again makes its appearance as soon as another drop of solution of perchloride of iron is added. The solution of protochloride of uranium, however, keeps the iron in the state of protoxide as long as the solution is still greenish. Consequently when a solution of perchloride of iron is mixed with so much protochloride of uranium that it is distinctly green, we may so completely reduce the perchloride of iron to protochloride, which is permanent for a considerable time in the air, that no precipitate of iron is obtained with carbonate of ammonia; carbonate of ammonia dissolves the protocarbonates of iron and uranium, and when only so much of the latter has been added as to render the solution distinctly green, we may in this way separate iron from bodies which are insoluble in alkaline carbonates, without the necessity of preventing the access of air.

In analyses we very frequently have to determine protoxide of iron in the presence of peroxide. This may probably be effected by means of solution of protochloride of uranium. Uranium itself is determined most exactly as perphosphate, which supports a red heat, without being in the least reduced to protoperoxide.—*Chemisches Centralblatt*, No. 11, March 18, 1857, p. 162.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On some new Products from the Compounds of Aldehydes with Bisulphite of Ammonia. *By* T. PETERSEN.

THE formation of nitrogenous volatile bases from compounds of the aldehydes with bisulphite of ammonia when heated with lime, has been often observed. In the fatty acid series, Gössmann has prepared the æthylamine of the benzoic acid group from the bisulphite of aldehyde-ammonia, amarine and lophine from the bisulphite of ammonia and *oil of bitter almonds*, and triphenylamine from the same double compound of cinnamic aldehyde*. The author has undertaken some further investigations of this subject in Wöhler's laboratory, under the special guidance of Gössmann.

Amongst the aldehydes of the fatty acid group, œnanthole is most readily obtained in large quantities. From the compound of this with bisulphite of ammonia, the author succeeded in obtaining tricapronylamine. As in the formation of this base a decomposition had taken place of such a kind that the radical œnanthyle had been converted into the next lower one by the elimination of 2 atoms of carbon as carbonic acid, the question arose, as to whether the compound regarded as æthylamine was not bimethylamine.

Both possess the same empirical formula, so that nothing but a substitution experiment could decide between them. The investigation of the bisulphite of aldehyde-ammonia was therefore again undertaken by the author in common with Gössmann; and besides a series of interesting products of decomposition, bimethylamine has been detected. At the same time a bisulphite of aldehyde-ammonia has been prepared, which differs in many of its properties from the well-known salt of Redtenbacher.

The Base obtained from the Bisulphite of Œnanthole-ammonia and its Compounds.—Œnanthole was first prepared by Bussy, he having ascertained that the fluid passing over during the distillation of castor oil was the aldehyde of the œnanthylic acid obtained by the oxidation of this oil with nitric acid. Williamson and Tilley subsequently obtained this acid from the aldehyde by the action of hydrate of potash.

The compound of œnanthylaldehyde with bisulphite of ammonia described by Tilley, was the second known double compound

* See Chem. Gaz., vol. xiii. p. 144.

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of this kind, after Redtenbacher had prepared the bisulphite of aldehyde-ammonia. Bertagnini then showed that the aldehydes universally possess the property of forming crystallizable compounds with bisulphite of ammonia.

The following was the process adopted for the preparation of the bisulphite of œnanthole-ammonia. A considerable quantity of castor oil was distilled in a spacious retort until the mass solidified in a resinous form, with strong effervescence, and the odour of acroleine made its appearance. At this time about one-tenth of the weight of castor oil employed had passed over, as is also stated by Bussy, consisting of œnanthole of a somewhat yellowish colour, and with a strong odour of adherent acroleine. If the residue be further heated, it again melts together, but no more œnanthole is obtained; essentially only hydrocarbons pass over.

The product obtained was poured into a perfectly saturated solution of bisulphite of ammonia, when the entire mass solidified into a thick crystalline paste under strong evolution of heat. The compound was washed with alcohol, in which it is nearly insoluble, and dried between paper, after which the odour of acroleine had nearly disappeared. In order to obtain it perfectly pure, however, it was again macerated with alcohol, pressed between paper, and dried. It now forms a finely laminar mass, which has a nacreous lustre, is fatty to the touch, and possesses a fatty odour. Its composition is—

$$C^{14} H^{14} O^{2}, NH^{3} S^{2} O^{4}.$$

The author performed the heating with lime in exactly the same way as described by Gössmann, and indeed with small quantities of 15 grms.

It was found most advisable to mix the compound with three times the quantity of caustic lime and the same of hydrated lime; a little caustic lime was put upon the bottom of the retort, and the mixture was also covered therewith. If the amount of caustic lime be increased, too large a quantity of resinous products is obtained in the distillate, which renders the preparation of the base in a pure state extraordinarily difficult; but if too much hydrated lime be employed, a great quantity of water passes, the amount of base turns out less, considerable quantities of unaltered aldehyde are found, and even œnanthylic acid is formed in small quantity. In the latter case, the large quantity of water evaporating renders the elevation of the temperature difficult, and the hydrate of lime is not enabled to exert its oxidizing action upon the aldehyde.

It is very essential to expose the retort coated with clay to a strong fire at the commencement of the operation, so that it may be partly surrounded with red-hot coals. If this be neglected, the base obtained is contaminated with hydrocarbons. During the distillation, an oil of an unpleasant odour goes over in abundance; this is at first colourless, but soon becomes yellow and brown with access of air. It floats upon an aqueous fluid.

The evolution does not continue very long, the strong odour disappears, and brown resinous drops make their appearance in the

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distillate. As these products of decomposition are very difficult to separate from the base during its rectification, the operation was interrupted as soon as they showed themselves. The residue in the retort contains sulphate and sulphite of lime, sulphuret of calcium, and carbonate of lime. Sulphurous acid, as is well known, is partially decomposed in the presence of strong bases at a high temperature into sulphuric acid and sulphur. There was also usually a little carbonized matter, formed in consequence of the high temperature.

The aqueous part of the distillate was separated from the oil by means of a moistened filter, and the filtrate reduced to dryness after neutralization with muriatic acid. Besides some sulphite of ammonia, which always passes over in small quantity, the solution could only contain ammonia and a soluble amine base. Nothing was taken up from the evaporated salt by absolute alcohol and æther. On testing, it proved to be nothing but muriate of ammonia.

The oily fluid was then treated in the following way. It was first of all digested at a gentle heat for some time with a solution of carbonate of soda, in order to convert the adherent œnanthole into œnanthylic acid and combine it with alkali, but especially to get rid of the ammonia; it was then washed with water upon a wet filter. As the compound is rapidly altered in contact with the air, the rectification was performed in a current of hydrogen. A brown resin remained in the retort. The body thus obtained is the purified base—

Tricapronylamine, $C^{36}H^{39}N$, a pale yellow fluid, which exhibits internal dispersion of light in a high degree, and shows a green tinge by reflected light. It possesses a peculiar, somewhat ammoniacal odour, has an alkaline reaction and taste, and produces a peculiar irritation in the throat. It is insoluble in water, but dissolves readily in an equal volume of alcohol, and still more easily in æther. It is lighter than water, burns with a luminous smoky flame, and boils at about 500° F. Salts of iron and alumina are precipitated by it, but the precipitate produced in the latter is again dissolved; it does not appear to be capable of expelling ammonia from its salts. It is but slightly soluble in aqueous acids, and combines with them to form salts, which are all deliquescent, and are rapidly altered, like the base itself, by contact with the air.

The analysis of the substance, protected as much as possible from the access of air and enclosed immediately after its preparation, but still not perfectly pure on account of its ready decomposability, gave the following results:—

C	81·49	80·98	81·196	36	80·3
H	13·33	14·177	13·956	39	14·49
N	5·02	..	..	1	5·21

From analogies in the series of fatty acids, this base may be appropriately characterized as a nitrile base as follows:—

$$\left.\begin{matrix} C^{12}H^{13} \\ C^{12}H^{13} \\ C^{12}H^{13} \end{matrix}\right\} N.$$

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If this view were correct, this nitrile base ought to be capable of conversion into an ammonium base by Hofmann's method of substitution by means of the iodide of an alcohol radical; this was effected by treatment with iodide of æthyle.

Protiodide of Tricapronylæthylammonium, $C^{36}H^{39}, C^4H^5N, I$.—Several portions of pure base were enclosed with an excess of dehydrated iodide of æthyle, in which the body dissolves with the greatest ease, and heated to 212° F. in the water-bath. On the second day the fluid had already acquired a dark red colour, and after this underwent no further change. At ordinary temperatures the action took place gradually, and several weeks were required for its completion.

The excess of iodide of æthyle was then evaporated as much as possible under the air-pump, and the mass remaining was gently heated for some time until no more iodide of æthyle was volatilized. The compound, which had a neutral reaction, formed a thick syrup of a cherry-red colour at ordinary temperatures; when heated to 86°–104° F., it again became fluid; it possessed a penetrating odour. When heated above 248° F., it slowly gave off vapours of iodine. It is readily soluble in alcohol and æther.

When the iodine was removed by means of hydrated oxide of silver with the aid of heat, and the base extracted by alcohol from the mass, no solid salt adapted for analysis could be prepared with muriatic acid and bichloride of platinum. By this treatment the compound was for the most part resinified. The analysis of the iodide gave the following results:—

C	57·67	40	56·52
H	9·84	44	10·35
N	..	1	3·29
I	29·24	1	29·84

These numbers show that by treatment with iodide of æthyle, the nitrile base, $C^{12}H^{13}, C^{12}H^{13}, C^{12}H^{13}, N$, had been converted into the iodide of the ammonium base, $C^{12}H^{13}, C^{12}H^{13}, C^{12}H^{13}, C^4H^5, N$.

It is also possible to prepare tricapronylamine in another way. The bisulphite of œnantholammonia was heated in the oil-bath in a sealed tube. When the temperature was raised to 482°–518° F., a complete alteration occurred in the compound. A crystalline salt had attached itself to the walls of the tube, which proved to be essentially sulphate of ammonia; sulphur had been deposited, and on opening the tube the odour of sulphurous acid was perceptible. A strong acid set free sulphurous acid and some carbonic acid, and the high temperature had also caused the separation of a little carbon. Together with these bodies there was an abundance of an oily fluid, which was mixed with some hydrate of potash, and purified by distillation. The fluid thus obtained possessed all the properties of the above-described base.

The compounds of tricapronylamine are deliquescent, and form oily drops or syrupous masses, some of which are lighter and some heavier than water.

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Muriate of Tricapronylamine, $C^{36}H^{39}N$, HCl.—When the alcoholic solution of the base is mixed with muriatic acid, the fluid becomes turbid, acquires a red colour, and separates oily drops on the surface; these gradually become converted into a thick brown resin. This body, muriate of tricapronylamine, is but slightly soluble in water, dissolves readily in alcohol and æther, but could not by any means be obtained in a solid form. To obtain as pure a compound as possible, the base, rectified in a current of hydrogen, was collected in a Liebig's bulb-apparatus, and exposed immediately to a current of thoroughly dried muriatic acid gas. The portion of the apparatus standing in connexion with the air was also protected from moisture by a chloride of calcium tube. The action of the muriatic acid gas was rapid; the mass became considerably heated and thick, and acquired a dark red colour. After the completion of the action, the excess of muriatic acid gas was displaced by hydrogen, for which purpose a long evolution of the latter was necessary, and finally the apparatus was heated first by hot water, and afterwards by a small spirit-lamp, to 212°–248° F. until no more acid vapours could be detected. The analysis of the compound thus obtained gave the following numbers:—

C	..	36	70·7
H	...	40	13·09
N	4·33	1	4·58
Cl	11·12	1	11·63

Platinochloride of Tricapronylamine, $C^{36}H^{39}N$, HCl, $PtCl^2$.—When an alcoholic solution of bichloride of platinum is mixed with an alcoholic solution of the muriate of the base, a thick yellow precipitate is thrown down instantaneously, but gradually disappears again, whilst the fluid acquires a dark colour, and a resin is deposited. The solution was therefore further diluted with alcohol, so that on the addition of bichloride of platinum no precipitate was produced immediately, and the whole was allowed to evaporate over sulphuric acid *in vacuo*, or in a space protected from the access of air. In a short time yellow crystalline masses, contaminated by a brown resin, had separated. When anhydrous æther was poured over the mass after the removal of the mother-liquor, it took up the impurities, and beautiful yellow laminæ were left; these were washed with æther and dried.

On one occasion crystals were obtained at once from the alcoholic solution, in the form of large, nearly colourless laminæ, which were employed for two platinum determinations.

The pure double salt forms silky, yellow or orange-red laminæ. It is pretty readily soluble in water, especially when hot, and also in ordinary alcohol; it dissolves with more difficulty in absolute alcohol, and is almost insoluble in æther. The solutions possess an exceedingly fine violet colour. If the crystals be heated above 392° F., they become black and decomposed; when pure, they remain unaltered by keeping, but when not well washed with æther, resinification easily takes place. The analyses were as follows:—

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C	45·07	44·72	36	45·46
H	8·18	8·051	40	8·41
N	..	..	1	2·95
Cl	..	..	3	22·41
Pt	21·01	20·81	1	20·77

In order to obtain the platinum double salt in a crystalline form from its solutions, an excess of acid must be avoided as much as possible, as otherwise the salt separates in the form of a resin.

Sulphate of Tricapronylamine.—From the alcoholic solution of tricapronylamine, sulphuric acid separates oily drops, which sink to the bottom. These are the sulphate.

An alcoholic solution of bichloride of mercury also separates an oil from the solution of the base in muriatic acid; this is heavier than water. It dissolves easily in alcohol and æther; in the ætherial solution, white tenacious masses are formed, which deliquesce in the air.

Sulphurous acid, conducted through the pure base or its alcoholic solution, is strongly absorbed, but a great part of it evaporates again rapidly.—From the Author's *Inaugural Dissertation*, Göttingen, 1857.

On a new Oxide of Silicium. *By* Prof. Wöhler.

In the course of some observations on the conducting power of aluminium for the electric current, MM. Wöhler and Buff found that if this metal be immersed as the positive pole in a solution of chloride of sodium, a gas is evolved which inflames spontaneously in the air, and when mixed with oxygen causes a strong detonation. Supposing this to be formed from silicium contained in the aluminium, they endeavoured to produce it in a purely chemical way. By heating silicium to a slight red heat in a dry current of muriatic acid gas, the latter was readily decomposed, furnishing hydrogen gas and a new chloride of silicium. This is a very mobile fuming liquid, more volatile than the ordinary chloride, $SiCl^3$. Water decomposes it into muriatic acid and a new oxide of silicium. The latter is a white substance, slightly soluble in water, and very soluble in alkalies, even in ammonia, evolving hydrogen gas with effervescence, and becoming converted into silicic acid. When heated in the air, it ignites, and burns with a very white light, evolving hydrogen, which inflames.—*Comptes Rendus*, April 20, 1857, p. 834.

Upon Amide Compounds of Molybdenum. *By* D. K. Tuttle.

The great similarity between tungsten and molybdenum rendered it probable that the latter would form with nitrogen similar compounds to those discovered by Wöhler* in the case of tungsten.

Pure sublimed molybdic acid was heated almost to ignition in a glass tube, in a current of dried ammoniacal gas, as long as water

* Liebig's Annalen, lxxiii. p. 190.

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was formed. The crystals, without changing their form, became dark purple, partly black, with a semi-metallic lustre. To extract any remains of unaltered molybdic acid, the substance was digested with concentrated ammonia, washed, and dried.

When solution of potash was poured over it, it evolved no ammonia; but when fused with hydrate of potash, it evolved a large quantity of ammonia, with formation of colourless molybdate of potash. Heated to redness in a current of dry hydrogen, it furnished gaseous ammonia, but also water, proving that it still contained oxygen.

When molybdic acid was heated to full redness in gaseous ammonia, it was completely reduced to the metallic state; it then, like tungsten, possessed the property of decomposing the ammoniacal gas with great ease into nitrogen and hydrogen.

The amount of molybdenum in the body obtained in the first experiment was determined by converting it into molybdic acid, by heating it in a current of oxygen and weighing the acid. Loss by volatilization was prevented by a plug of asbestos in the tube. A small quantity of water made its appearance. 92·9 per cent. of molybdic acid were found, agreeing with a nitruret of molybdenum of the formula $Mo^4 N$, which requires 93 per cent. The compound probably consists essentially of $Mo^3 N$, but contains intermixed metallic molybdenum. By the employment of a higher temperature, only 77·9 and 73 per cent. of molybdenum and 0·18 per cent of hydrogen were obtained. No more constant result was obtained by heating molybdate of ammonia in gaseous ammonia.

The author then prepared a body which had hitherto been regarded as peroxide of molybdenum, by fusing in a crucible a mixture of molybdate of ammonia and muriate of ammonia under a covering of chloride of sodium. The black mass obtained was treated alternately with water, dilute solution of potash, and muriatic acid, well washed and dried. The product was a bluish-black powder, which evolved a considerable amount of ammonia when fused with hydrate of potash. It was evidently a mixture containing oxide, which yielded on an average 80 per cent. of molybdenum, and curiously enough hydrogen, besides nitrogen and oxygen.

When perchloride of molybdenum, $MoCl^2$, was heated in dry gaseous ammonia to a temperature just sufficient to volatilize the muriate of ammonia formed, a black caked mass, with a metallic lustre on the glass, was obtained, exactly like that formed with perchloride of tungsten. This body evolves no ammonia with solution of potash, but ammonia is formed immediately in abundance when it is fused with hydrate of potash. It is not changed by muriatic acid, but is immediately dissolved as molybdic acid by nitric acid. It is also dissolved by hypochlorite of soda, with evolution of nitrogen gas. When heated in the air, it ignites, and smoulders away to molybdic acid. When heated to redness in a tube, it evolves ammonia. In analysis by combustion in oxygen gas, water is formed. 82·83 per cent. of molybdenum were found. If it had been merely nitruret of molybdenum of the formula $Mo^3 N$, it should have con-

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tained 90·7 per cent. of metal. Its composition therefore is probably analogous to that of the tungsten compound formed in the same way = $Mo^2N + MoNH^2$, which requires 82·1 per cent. of metal.—Liebig's *Annalen*, March 1857, p. 285.

Researches on the Ammonia-cobalt Bases.
By WOLCOTT GIBBS *and* F. A. GENTH.

[Continued from page 176.]

Purpureocobalt.

The salts of purpureocobalt are often found among the direct products of the oxidation of ammoniacal solutions of cobalt. They are often formed from the salts of roseocobalt by heating or by boiling with strong acids, the cobalt passing, as we conceive, from one modification to another. The salts of purpureocobalt are also formed in great abundance by the action of acids upon salts of xanthocobalt; and we are disposed to think that they may also occur, though rarely, among the products of the decomposition of salts of luteocobalt.

The salts of purpureocobalt are distinguished by a fine violet-red or purple colour, which is common to nearly all of them, and which is very different from the comparatively dull red of the salts of roseocobalt. They are in general somewhat less soluble than the compounds of roseocobalt, and crystallize for the most part in well-defined crystals. When neutral, they have a purely saline non-metallic taste.

Heat readily decomposes the salts of this base; the final products of the decomposition are the same as in the case of the salts of roseocobalt, but intermediate products are often formed. The neutral solutions are readily decomposed by boiling, the products of the decomposition being a black or dark brown oxide of cobalt and a salt of ammonium, free ammonia being given off. In some cases, however, salts of luteocobalt are intermediate products of this decomposition.

All the salts of purpureocobalt, by long boiling with an excess of hydrochloric acid, yield the chloride.

Chloride of Purpureocobalt.—The substance which we shall describe under the name of chloride of purpureocobalt, is the same as that to which Fremy gave the name of chloride of roseocobaltiaque. In the course of our investigations it at length became clear, that, under the name of salts of roseocobalt, the compounds of two perfectly distinct bases have hitherto been confounded. It became, therefore, necessary to devise a new name. The purple colour of the salts which correspond to the chloride now to be described, led us to adopt the name of purpureocobalt for the radical of these salts, as more appropriate than roseocobalt, which we have retained for most of the salts to which it was originally applied. Such a change is to be regretted; it could not, however, have been avoided without an introduction of two entirely new names.

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We have already stated that the chloride of purpureocobalt is often a product of the direct oxidation of an ammoniacal solution of the chloride of cobalt exposed to the air. In these cases it is sometimes mixed with chloride of roseocobalt, and sometimes forms the entire product of the oxidation. We believe that the temperature at which the process of oxidation goes on is the condition which determines the character and the amount of the chloride which is formed during the oxidation. The chloride of roseocobalt is, in our view, the first product of the oxidation under all circumstances. At a moderately high temperature, however, the chloride passes as fast as it is formed into chloride of purpureocobalt, which may thus be the only final product of the oxidation, or may be mixed with variable proportions of the chloride of roseocobalt.

In one experiment made during the summer season, and in which chemically pure chloride of cobalt and ammonia were employed, the process of oxidation went on very slowly, without the precipitation of any trace of sesquioxide of cobalt. The liquid had a dull purple colour, and gave with reagents no precipitates or reactions to indicate the presence of chloride or oxide of purpureocobalt or roseocobalt. On boiling with hydrochloric acid, however, the chloride of purpureocobalt was thrown down in abundance, and no other substance could be detected in the supernatant liquid. In this case the oxidized liquid gave no precipitate with hydrochloric acid in the cold, but the cold solution, after some hours' standing, deposited distinct crystals of chloride of purpureocobalt. We believe that in this case a combination of the oxide and chloride existed in the solution, so that, as we have already suggested in speaking of the chloride of roseocobalt, the oxidation itself would be expressed by the equation—

$$6CoCl + 15NH^3 + 3O = 5NH^3 . Co^2 O^3 + 2(5NH^3 . Co^2 Cl^3).$$

If we admit that the oxide and chloride of purpureocobalt as thus formed are actually in combination so as to form a sort of oxychloride, and are not merely mechanically mixed, we may perhaps explain why no precipitates of salts of purpureocobalt are obtained in the oxidized liquid, since the reagents added might not be able to overcome the affinity between the oxide and chloride. It is easy to see that by boiling with hydrochloric acid, the combination of oxide and chloride will give the chloride alone, since we may have the equation—

$$5NH^3 . Co^2 O^3 + 2(5NH^3 . Co^2 Cl^6) + 3HCl = 3(5NH^3 . Co^2 Cl^3) + 3HO.$$

We have already mentioned that the chloride of roseocobalt is readily converted into chloride of purpureocobalt, by boiling with hydrochloric acid, or even by gently heating its solution. This circumstance explains why only the chloride of purpureocobalt is obtained by boiling a completely oxidized ammoniacal solution of chloride of cobalt, even when this solution contains only roseocobalt, or a mixture of roseocobalt and purpureocobalt. It also enables us to understand why all writers upon the ammonia-cobalt bases, up to

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the period of the present investigation, entirely overlooked the chloride of roseocobalt, and consequently described the salts of that base, as if they corresponded to, and contained the same radical as, chloride of purpureocobalt.

It is not necessary to add chloride of ammonium to the ammoniacal solution of chloride of cobalt, in preparing the chloride of purpureocobalt. It is, however, advantageous to do so, because the oxide of purpureocobalt is converted by it as fast as formed into the chloride, and the formation of the oxychloride is prevented. To prepare the chloride of purpureocobalt in a pure state from the oxidized liquid, it is only necessary to boil this with an excess of hydrochloric acid. A crimson powder is thrown down, while the supernatant liquid becomes nearly colourless, provided at least that a pure salt of cobalt was employed, and that the oxidation was complete. The mother-liquor is to be poured off, and the precipitate dissolved in a large quantity of boiling-water, to which enough hydrochloric acid has been added to render the solution distinctly acid. On cooling, the solution gives small but beautiful crystals of the chloride, almost perfectly pure. A second crystallization usually removes all traces of impurity. It is not, however, necessary to use a pure chloride of cobalt in preparing the chloride of purpureocobalt. Any commercial oxide will answer, even when arsenic, nickel, iron, &c. are present. On the other hand, it is easy to prepare a perfectly pure chloride of cobalt, by heating the chloride of purpureocobalt in a porcelain crucible until vapours of ammonia and chloride of ammonium cease to be given off. The pure chloride of cobalt thus obtained is remarkable for its beauty of colour, the anhydrous chloride forming pale blue talcose scales, while the solution and the crystals obtained from this have a very fine violet-red tint.

The chloride of purpureocobalt may be prepared by other methods. One of the most interesting of these is, by the action of strong hydrochloric acid upon a salt of xanthocobalt. It is almost a matter of indifference which salt of xanthocobalt is employed. As, however, the nitrate is, perhaps, most easily obtained in a pure state, it is usually most advantageous to employ this. The nitrate has the formula—

$$NO^2.5NH^3.Co^2O^3, 2NO^5 + HO.$$

On boiling with hydrochloric acid, the salt is slowly converted from a brown-yellow to a lilac-purple powder, which is insoluble in the supernatant acid liquid. After boiling strongly for an hour or two, almost all the original salt is decomposed, NO^2 is given off in abundance during the boiling, while a lilac-coloured uncrystallized mass remains at the bottom of the flask. The supernatant liquid is to be poured off, and boiling water added to the insoluble portion. A brown-yellow or dark sherry-wine coloured solution is usually formed, which is again to be poured off, and the washing repeated till the liquid has a clear purple colour. The red mass is then to be dissolved in boiling water, to which a little hydrochloric acid has been added, and filtered. On cooling, the chloride of purpureocobalt crystallizes in small brilliant crystals, which must be repeatedly

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recrystallized to separate all traces of impurity. The washings, on boiling with hydrochloric acid, yield a fresh portion of the chloride. The reaction which takes place under these circumstances may be expressed by the equation—

$$NO^2.5NH^3.Co^2O^3, 2NO^5+3HCl=NO^2+2NO^5, HO+5NH^3.Co^2Cl^3+HO.$$

As already remarked, the chloride or sulphate of xanthocobalt may be employed in a precisely similar manner, and also yield the chloride of purpureocobalt. When the sulphate is used, however, the resulting chloride is apt to retain sulphuric acid with much obstinacy, and can with difficulty be freed from it.

Another method of preparing the chloride of purpureocobalt, consists in boiling the chloride or nitrate of roseocobalt with hydrochloric acid. This method is very convenient, and yields a very pure chloride.

The chloride of purpureocobalt may also be prepared by boiling the acid sulphate of this base with hydrochloric acid. In this case, however, as in all others in which sulphuric acid is present in the solution, the chloride should be boiled with a little chloride of barium, and repeatedly recrystallized, to separate traces of the isomorphous sulphate of roseocobalt formed at the same time.

The chloride of purpureocobalt has a beautiful violet-red or purple colour, and is dichrous, the ordinary ray being colourless, while the extraordinary ray has a rich violet-red tint. Its solution is violet-red. The salt is nearly insoluble in cold water, but is soluble without decomposition in boiling water to which a few drops of hydrochloric acid have been added. From this solution it separates on cooling in very brilliant small crystals, which are simpler in form the purer the solution from which they have crystallized. The crystals belong to the square prismatic or dimetric system, according to Prof. Dana, and not to the regular system, as stated in previous memoirs. The observed forms are the octahedron and first and second prism.

The crystals are usually small, but extremely well formed; those which are obtained from solutions containing a little chloride of mercury most frequently exhibit the planes of the first and second prism, and are larger than those which separate from pure solutions. From the measurements, it appears that the chloride of purpureocobalt is isomorphous with the sulphate of roseocobalt. This isomorphism is the more remarkable, inasmuch as a precisely similar case occurs with the chloride and sulphate of luteocobalt, between which there is a similar difference of constitution. Thus we have—

$$5NH^3.Co^2Cl^3=5NH^3.Co^2O^3, 3SO^3+5HO$$
$$6NH^3.Co^2Cl^3=6NH^3.Co^2O^3, 3SO^3+5HO.$$

From this it appears that in both cases we have the crystallographic equality—

$$3Cl=O^3, 3SO^3+5HO.$$

The density of the crystals of chloride of purpureocobalt, as taken in alcohol, is 1·802 at 23° C.; the atomic volume of the chloride is consequently 139·0.

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The chloride of purpureocobalt has the formula $5NH^3 . Co^2 Cl^3$, which requires—

	Equivs.		Theory.	Mean.		Found.		
Cobalt....	2	59	23·55	23·56	23·58	23·57	23·55	23·55
Chlorine..	3	106·5	42·50	42·43	42·49	42·31	42·52	42·40
Hydrogen	15	15	5·98	6·11	6·04	6·19	6·10	6·11
Nitrogen..	5	70	27·97	28·01	28·05	27·93	28·12	28·11

The agreement of these analyses leaves no reasonable doubt that the true formula of the chloride of purpureocobalt is $5NH^3 . Co^2 Cl^3$, as first correctly determined by Rogojski, and subsequently by Gregory. Fremy gives in addition 1 equiv. of water, while Claudet makes 16 in place of 15 equivs. of hydrogen. That the salt, however, contains but 15 equivs. is clear, from the fact that free nitrogen and hydrogen are found among the products of its decomposition by heat in an atmosphere of carbonic acid gas, which could not be the case upon Claudet's view, since we should then have the equation—

$$N^5 H^{16} Co^2 Cl^3 = 5NH^3 + 2CoCl + HCl,$$

while the presence of free nitrogen and hydrogen renders it probable that the decomposition is in reality expressed by the equation—

$$5NH^3 . Co^2 Cl^3 = 2CoCl + NH^4 Cl + 3NH^3 + N + 2H.$$

We have more than once endeavoured to determine the amount of gas actually given off during this decomposition, with the view of verifying the equation just given. In every case, however, a portion of the chloride of cobalt was reduced, either by the free ammonia or by the hydrogen, so that much metallic cobalt was found mixed with the chloride. A neutral solution of the chloride of purpureocobalt is readily decomposed by boiling, a dark brown precipitate, probably of the hydrated magnetic oxide, being thrown down, while the solution becomes brown-yellow, and contains chloride of ammonium and chloride of luteocobalt, ammonia being at the same time given off. The quantity of chloride of luteocobalt which is thus formed is always very small, being very much less than 1 equiv. for 2 equivs. of the chloride of purpureocobalt.

On the other hand, a solution of chloride of purpureocobalt may be boiled for a very long time with concentrated hydrochloric acid without decomposition; and this stability in the presence of acids is one of the most remarkable peculiarities of the whole class of ammonia-cobalt bases.

Hydrochloric acid and the alkaline chlorides precipitate chloride of purpureocobalt from its solutions almost completely, slowly in the cold, but instantly on boiling. Ignited in a current of hydrogen, the salt yields metallic cobalt as a gray spongy mass. Heated in an open crucible, the salt fuses and swells up, giving off abundant vapours of chloride of ammonium and ammonia, while pure chloride of cobalt remains in lavender-blue scales. In some cases, however, this is mixed with metallic cobalt, while in others, in which the ignition takes place with free access of air, brilliant iron-black

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octahedra are formed, which are the anhydrous magnetic oxide of cobalt, $Co^3 O^4$. The red gas arising from the action of nitric acid upon starch or sawdust exerts a very remarkable influence upon the chloride of purpureocobalt, converting it into the nitrate of a base, which will be described further on under the name of xanthocobalt.

Sulphurous acid solution throws down from solutions of the chloride a dull orange-brown precipitate, which appears to be a sulphite. By boiling with an excess of the acid, this is reduced, and there remains a solution of a protosalt of cobalt.

Sulphuric acid, under certain conditions, converts chloride of purpureocobalt into the acid sulphate of the same base.

Zinc may be boiled a long time with an acid solution of the chloride, without producing decomposition or reduction. Formic and oxalic acids have no reducing action. Protochloride of tin simply unites with the chloride of purpureocobalt so as to form a chloro-salt.

The chloride of purpureocobalt exhibits a remarkable tendency to unite with metallic chlorides to form chloro-salts. Such compounds are formed with the chlorides of platinum, palladium, mercury, tin, zinc, and various other metals. The chloride of purpureocobalt even dissolves chloride of silver in large quantity, doubtless forming with it a double chloride. It is for this reason, that it is not generally advantageous to prepare the salts of purpureocobalt by double decomposition between the chloride and salts of silver.

The reactions of a pure solution of the chloride of purpureocobalt are as follows:—Ferrocyanide of potassium gives a yellowish precipitate, which quickly becomes chocolate-brown. Ferridcyanide of potassium gives a beautiful, bright orange-red, crystalline precipitate. Cobalticyanide of potassium gives a fine red crystalline precipitate. Oxalate of ammonia gives a beautiful purple-red precipitate of fine needles. Pyrophosphate of soda gives a lilac precipitate, easily soluble in an excess of the precipitant. Neutral chromate of potash gives a brick-red precipitate. Bichromate of potash gives orange-yellow scales. Picrate of ammonia gives a beautiful yellow precipitate. Terchloride of gold precipitates the chloride unchanged. Bichloride of platinum gives a fine cinnamon-brown precipitate of crystalline scales. Sulphide of ammonium gives a black precipitate. Chloride of mercury gives fine rose-red needles, easily decomposed. Bichloride of tin gives pale peach-blossom-red silky needles. Molybdate of ammonia gives a pale peach-blossom-red precipitate. Alkalies and their carbonates give no precipitate. Iodide and bromide of potassium give no precipitate. Hydrochloric acid and the alkaline chlorides throw down the chloride of purpureocobalt from its solutions as a violet-red powder.

The reactions of the chloride of purpureocobalt with the ferridcyanide and cobalticyanide of potassium and with oxalate of ammonia are not sufficient to distinguish it from the chloride of roseocobalt, which, when pure and freshly prepared, gives also precipitates with these reagents. The character of the precipitates with oxalate of ammonia, bichloride of platinum, and bichromate of potash enable

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us, however, readily to distinguish the chloride of purpureocobalt from chloride of roseocobalt, with which, however, it is not likely to be confounded.

[To be continued.]

On some Points in the Composition of Wheat-grain, its Products in the Mill, and Bread. By J. B. LAWES, F.R.S., F.C.S., *and* J. H. GILBERT, Ph.D., F.C.S.*

This paper discussed an extensive series of experiments, in which wheat-grain and its products were traced from the field to the bakery, the results being given in numerous Tables. The first of these gave a summary of the results of the growth of wheat for ten years consecutively on the same land, and illustrated the influence of variation of climatic circumstance from year to year in one and the same locality, upon the general character and composition of the crop. The conclusion the authors arrived at was, that within the limits of their own locality and climate, the season yielding the admittedly best character of grain, also generally afforded a high per-centage of dry substance in the grain, and comparatively low per-centages both of mineral matter and of nitrogen in that dry substance. The straw showed variations in these same points of composition, generally somewhat in the same direction as the grain, but was subject to a wider range of exceptions than the latter in this respect.

The influence of various conditions of *manuring* upon the character and composition of the crop was next considered. With this view, the results obtained upon individual plots during the same ten years were now given, instead of the average from many plots in each year, as when the effects of season alone were to be discussed. In the experiments illustrating the effects of manures, there was pretty generally a slight increase in the per-centage of nitrogen in the grain grown by an annual excess of ammoniacal salts, compared with that grown by its side on land which was continuously unmanured. In the average of the seasons, however, there was a somewhat lower per-centage of nitrogen in the grain, where there had been a liberal supply of the required mineral constituents also, than where the ammoniacal salts were used alone. The range of difference in the per-centage of nitrogen in the produce in one and the same season was, however, even with these extreme variations as to the available supplies within the soil, not nearly so great as it was in different seasons with one and the same condition of manuring.

Twenty-three analyses of wheat-grain *ashes* were next recorded; nine referring to grains grown by different manures in 1844, eight to similarly varying specimens the produce of 1845, and six to as many of 1846. From these it did not appear that the per-centage of any particular constituent of the ash of the ripened grain was directly affected by the liberal use of it in manure. At any rate, the differences, if any, due to this cause, were within the limits of the ordinary errors of analysis. Here again, however, the effects of

* Quarterly Journal of the Chemical Society, April 1857. Read Jan. 19, 1857.

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varying season were more marked than those of various manuring. Thus it was shown, in a summary Table of the results of the ash-analyses, that the difference in the per-centage amount of almost every constituent was much the greatest among the several grain-ashes of 1845, which was a very bad ripening season, and much the least among those of 1846, which was the best maturing season of the three included in this comparison. It would thus appear that, other things being equal, the more favourably and perfectly matured the grain, the more constant would be the composition of the ash, and the less any direct effect upon it from the mineral supplies by manure. Taking together the mean of twenty-three analyses of the ashes of grains grown at Rothamsted, and that of twenty-six analyses of wheat-grain ashes published by Mr. Way, it appeared that this ash consisted essentially of phosphates of potash, magnesia, and lime. The phosphoric acid amounted to nearly 50 per cent., the potash to about 30, the magnesia to from 10 to 12, and the lime from 3½ to 4 per cent. in the crude ash. The remainder, excluding adventitious sand and charcoal, consisted of small but variable amounts of soluble silica, peroxide of iron, and soda or chloride of sodium; with, according to Mr. Way, occasional traces of sulphuric and carbonic acids also. Soda or chloride of sodium seemed to abound much more in the ash of the less favourably ripened specimens; and the results afforded no reason for supposing that soda could take the place of potash as a constituent of the ash of fully developed grain.

In selected cases, quantities of experimentally grown grains, namely, seven lots from the produce of 1846, nineteen from that of 1847, and two from that of 1848, were carefully watched through the milling process. In some of the cases nine, and in others seven different products of the dressing apparatus, were separately taken. The proportion of each of the several products in the respective grains was ascertained and recorded, and the per-centages of dry substance and mineral matter were also in every case determined. The three first wires of the dressing machine gave on the average rather more than 70 per cent. of the grain as *fine* flour; but in practice about 10 per cent. more would be obtained from the next two products, yielding in all 80 per cent. or more of pretty good bread-flour. The average amount of *dry substance* in the various mill-products was about 85 per cent.; the external or more branny portions containing rather more, and the finer flours rather less. The per-centage of mineral matter varied very much in the different products, it being scarcely three-fourths of 1 per cent. in the fine flours, and ten times as much, or more than 7 per cent., in the coarsest bran. From the much larger proportion of flour than bran, however, it resulted that rather more than one-third of the total mineral matter of the grain would be accumulated in its currently edible portions.

In one series of these mill-products, from the finest flour at the head of the machine down to the coarsest bran, the nitrogen was determined, and also some of the constituents of the respective ashes.

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It appeared that the per-centage of nitrogen was about once and a half as great in the bran as in the finer flours. And even including all the currently edible portions, still the excluded branny parts contained considerably higher per-centages of nitrogen. Turning to the ashes of the respective mill-products, there was a much larger proportion of matter insoluble in acid in those of the finer flours than in those of the coarser brans; of the *phosphoric acid*, on the other hand, there was considerably the higher per-centage in the ash of the brans. The magnesia also was the higher in the ash of the brans, and the potash and lime the higher in that of the flours. Looking to the *distribution* of the various constituents, according to the average proportion in the grain, of each of the several mill-products, it appeared that about three-fourths of the total *nitrogen*, and about one-third or two-fifths of the total *mineral matter*, were accumulated in the usually edible flours, and of the total phosphoric acid there was only about one-third in the ashes of the latter. Notwithstanding the higher per-centage of nitrogen, and the large actual amounts of the mineral constituents of the grain contained in the branny portions, the authors were of opinion, that, besides the information at present at command as to the character and condition of the nitrogenous constituents of the bran, such were the effects of the branny particles themselves in increasing the peristaltic action, and thus clearing the alimentary canal more rapidly of its contents, that it was questionable whether frequently more nutriment would not be lost to the system by the admission into the food of the imperfectly divided branny particles, than would be gained by the introduction into the body coincidently with them of the larger amount of supposed nutritious matters. The action alluded to might indeed be conducive to health with those of a sluggish habit or who were overfed; but with those who were not so, the benefits derivable from an already perhaps scanty diet would be still further reduced.

Experiments were also described, in which several lots of the experimentally grown wheats were ground in a colonist's steel hand-mill. The results of the examination of the products thus obtained were in the main consistent with those from the products of the ordinary mill. They showed, however, more strikingly the effects of mechanical means in separating different chemical compounds within the limits of the floury part of the grain.

Experiments were next adduced, in which the different edible products, from grains grown by different manures or in different seasons, were made into bread; the several products of the dressing machine being employed sometimes separately and sometimes collectively. The result obtained was, that comparing with each other the three separate products which together yielded a fine flour, that from the head of the machine, which was the least nitrogenous, yielded on the average the least weight of bread for a given amount of flour, that is to say, it retained the least amount of water. Again, when the three products were mixed together, the flours of the season of 1846, which were the less nitrogenous, gave the less weight of bread, that is, retained less water than those of 1847, which were rather

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the more nitrogenous. The effect of an increase of nitrogen in augmenting the weight of bread was, however, not observable when this increase was due to including more of the more branny portions of the grain. The average yield of bread in twenty-two experiments with the individual products was rather more than 135 for every 100 of flour,—equal to about 63 per cent. of dry substance and 37 of water in the bread. The average of nineteen experiments with fine flour, composed of the products of the first three wires mixed together, gave a produce of about 137½ of bread for every 100 of flour, and about 61½ of dry substance, and 38½ of water in the bread. Bakers' loaves were next examined. Of these, four obtained from different bakers in the country gave an average of about 62 per cent. of dry substance and 38 of water in the bread; and three procured in London, rather more than 64 of dry matter and rather less than 36 of water. The authors concluded, that from 36 to 38 per cent. of water was perhaps the best average that could be assumed for bakers' *wheaten* bread within twelve hours of its being withdrawn from the oven. They showed, by reference to a Table of the results of other experimenters, that this agreed pretty well with the determinations of some of the most recent and trustworthy. Others, however, gave the water in bread as much higher; and all seem to agree that it was generally higher in country bread than in that of towns and cities.

The point next illustrated was the general influence of locality and varying climatic circumstance upon the per-centage of *gluten* in wheaten flour. It appeared by the numerous results adduced, that, other things being equal, there was a tendency to an increase in the per-centage of gluten, proceeding from the north to the south—a point which was illustrated in specimens both from the European and American continents. A comparatively high ripening temperature was indeed, among other circumstances, favourable to a high per-centage of gluten. There were, however, interesting exceptions to this generalization; at any rate, so far as the per-centage of the *nitrogen*, if not of the gluten itself, was concerned. Direct determinations of nitrogen, in numerous pairs of specimens contrasted as to locality, had however led to conclusions perfectly consistent in the main with those to which the quoted results as to gluten had conducted; whilst the results of others pointed in the same direction.

The foreign wheats containing a high per-centage of gluten, which were generally ripened under a high temperature, had the undoubted character of yielding a flour of great '*strength*,' and retaining a considerable amount of water in the bread. Owing, however, to their frequent hardness, and the peculiarity of their structural character generally, which rendered them both refractory in the mill, and less fitted to make an easily workable dough, and a bread of the desired colour, texture, and lightness, they were less valued to use *alone* for bread-making purposes than many grains of less *per-centage* of gluten, provided only that they were in an equal condition as to maturation or elaboration of their constituents. Some of the most approved foreign bread-flour grains in the market

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had indeed a comparatively low per-centage of nitrogen; but apparently a very high *condition* of both their nitrogenous and non-nitrogenous compounds, as well as a very favourable relation to each other of these two classes of constituents. Within the limits of our own Island, again, on the average of seasons, the better elaborated grain would probably be the less nitrogenous; though the nitrogenous matter it did contain would be in a high condition as to elaboration, and as to its mutual relations, structural and chemical, with the other constituents of the flour. Hence it came to pass, that as our home-grown flours go, those which were the best in the view of the baker would frequently be those having a comparatively low *per-centage* of nitrogenous compounds, a higher *condition* more than compensating for the higher per-centage of nitrogen, generally associated as it was in our climate with an inferior degree of development and maturation of the grain.

It was further maintained, that the high per-centage of nitrogen or gluten in wheaten flour was no more an unconditional measure of value to the *consumer*, than it was in the view of the baker.

In illustration of this latter point, a Table was given showing the relation of nitrogen to carbon in a number of current articles of food. It was submitted, that the underfed or chiefly bread-fed working man, would, as his means increased, generally first have recourse to the addition of bacon, or other highly fatty matters; which, though they might increase the actual amount of nitrogen consumed, would seldom increase, and frequently decrease, the *proportion* of the nitrogenous or flesh-forming to the more exclusively respiratory and fat-forming constituents. Indeed, so large was the amount of fat, and therefore of respirable hydrogen, as well as respirable carbon, even in fresh meat itself, that by its use the proportion of the nitrogenous to the other constituents would be much less augmented than might be generally supposed. Further illustrating the point by reference to the average relation of nitrogen to carbon in numerous dietaries, in many of which meat was included, and therefore fat with its respirable hydrogen as well as respirable carbon, the authors concluded, that, independently of cookery, that which was admitted to be a superior class of diet, was distinguished much more by including a certain amount of the more peculiarly respiratory and fat-forming constituents, in the condition and state of concentration as in fatty matter itself, and of the nitrogenous ones, in the high condition as in animal food, than by the higher proportion of the flesh-forming, to the more exclusively respiratory and fat-forming constituents.

Finally, in an Appendix* was given a Tabular Form, showing the relation of the yield, and composition of the bread, to that of the flour, according to the number of loaves obtained per sack (280 lbs.) of the latter. And, assuming it to be established that the loss of dry substance by fermentation was less than one, or perhaps less

* The Appendix was too late for insertion in the Journal of the Chemical Society, but the authors will be glad to forward a private copy to any one desiring it.

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than half of one per cent. of that of the flour employed, it resulted that the gain in the weight of bread by the non-fermenting method, was simply a gain in the water retained. Unless, therefore, the unfermented bread were better adapted for digestion and assimilation, or it were sold at a correspondingly lower price, the consumer would be a considerable loser by the purchase of the unfermented loaf.

On the Formation of Nitrous Acid from Ammonia.*

By D. K. Tuttle.

A blue solution produced from metallic copper and ammonia, exposed to the contact of air, had been left standing for several months, and become dried to a mass which resembled carbonate of copper in its appearance. When muriatic acid was poured over this, it effervesced strongly, and at the same time evolved an abundance of red fumes of nitrous acid. This led to the supposition that nitrous acid had been formed from the nitrogen of the ammonia.

To ascertain this, finely cut chips of very thin bright copper leaf were put into a dish, and concentrated ammonia was poured over them, so that both were still in contact with the air. The ammonia was free from nitrous or nitric acid. The dish was covered with a glass plate, and left standing for several days. The deep blue fluid produced was freed by heat from the excess of ammonia, mixed with pure sulphuric acid, and distilled, the vapours being collected in pure milk of lime. From this all the free hydrate of lime was precipitated by carbonic acid; the fluid was filtered, and carefully evaporated to dryness. A small quantity of a colourless deliquescent salt remained; this behaved like nitrite of lime. With sulphuric acid it evolved a quantity of yellowish fumes of nitrous acid.

A fluid containing more nitrous acid was obtained when ammonia was allowed to drop through a filter filled with fine bright strips of copper leaf, loosely stopped by a plug of asbestos, and the fluid passing repeatedly returned upon the copper. A similar, but not better, result was obtained when a mixture of aqueous vapour and gaseous ammonia were passed through a long tube filled with bright strips of copper; the mixture was obtained by passing air from a gasometer through pretty strong hot ammonia, and the progress of the action could be well observed.

To decide whether the formation of the nitrous acid only takes place after the oxidation of the copper, a solution of hydrated peroxide of copper in ammonia was prepared, and exposed to the air for some weeks. No trace of nitrous acid could be detected.

On the other hand, traces of this acid were formed when a colourless solution of protoxide of copper in ammonia was exposed to the influence of the air, and thus became blue. The quantity of

* The author remarks, with regard to what Prof. Schönbein has published upon this subject, that his observation was made last May, and that when this mode of formation of nitrous acid was mentioned to the Professor last summer in Göttingen, it was still unknown to him.

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acid formed was, however, so small, that it could only be detected by means of iodide of potassium and starch. The oxidation of the ammonia therefore takes place simultaneously with that of the copper, and is caused by this. According to Schönbein, we must suppose that in this case the copper converts the oxygen of the air into ozone.—Liebig's *Annalen*, March 1857, p. 283.

On the solid Fatty Acid in Cod-liver Oil. *By* Dr. Luck.

The inducement to this investigation was given by the turbid unsaleable residue of a ton of cod-liver oil, which had been set in a drying chamber in the expectation that the constituents which rendered it turbid would be dissolved by the aid of heat. This residue certainly became clearer after the first action of heat; but afterwards, when it remained exposed to a temperature of 41° F., it solidified by the separation of large crystalline laminæ, which filled the whole mass. All the fluid part was removed by draining and pressing, the pressed residue was saponified by potash, the soap was thrown down by common salt, precipitated with basic acetate of lead, and the lead-soap obtained extracted by means of æther until everything soluble was taken up.

The lead-salt was decomposed by muriatic acid, and the fatty acid separated taken up by alcohol; the solution was then purified with animal charcoal, and left to cool. The acid separated in a crystalline form, and was obtained pure by repeated crystallizations from alcohol. The author gives this acid the name of

Gadic Acid.—Its composition is $C^{29} H^{28} O^3 + HO$. It fuses at 145°–147° F., and solidifies at 140° F., acquiring a remarkable crystalline texture, by which it is distinguished from the other fatty acids. The author analysed the baryta-salt and the silver-salt. The potash-salt crystallizes from its solution in absolute alcohol, in large shining laminæ. Analysis:—

C	50·85	29	50·87
H	8·34	28	8·18
O	6·86	3	7·04
AgO	33·95	1	33·91

Further experiments showed that the solid body which caused the turbidity in the cod-liver oil was free gadic acid, and that this acid may be obtained by the saponification of clear oil.—*Neues Jahrb. für Pharm.*, vi. p. 249.

Analysis of Cadmium Amalgam. *By* C. R. König.

The cadmium amalgam, which has now for some time been employed with good results by the dentists, consists in 100 parts, of 25 parts cadmium and 74 parts of mercury. This agrees pretty well with the formula $Cd^5 Hg^8$. This amalgam is obtained by triturating an excess of cadmium with mercury.—*Journ. für Prakt. Chem.*, lxix. p. 466.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On some general Methods of preparing the Simple Bodies. *By* H. SAINTE-CLAIRE DEVILLE.

AFTER referring to the note of M. Brunner on the preparation of manganese*, and to a memoir of his own in the 'Annales de Physique et de Chimie,' the author states, that it is his opinion that the most certain process for obtaining manganese and chromium in a state of purity, consists in preparing them by means of a mixture of oxide and charcoal, in which the oxide predominates. It is necessary to fuse them in a vessel of lime and magnesia, and he prefers lime on account of its alkaline activity. Earthen or porcelain crucibles, as well as borax, are always partially reduced by the metals of this kind, and, which is curious, even by platinum. The silicium thus produced considerably increases the fusibility of the metal, and imparts to it a certain degree of brittleness. Charcoal vessels are of course excluded, if the formation of a pig metal is to be avoided. In a lime crucible the excess of oxide of chromium or manganese is absorbed by the lime, forming a manganite or chromite of lime, which is very difficult of fusion, but which removes all foreign bodies from the metallic ingot, especially silicium and carbon. Manganese and chromium, of which extreme hardness appears to be a distinctive property, then present this character in a very high degree. But the fusibility of the metals is sensibly diminished, so that, according to the author, pure chromium is less fusible than platinum.

If cobalt and nickel be prepared in this way, they are found to possess properties essentially different from those hitherto assigned to them. Cobalt is one of the most ductile and tenacious of known metals; a cobalt wire supports a weight almost double that which breaks an iron wire of the same thickness. Nickel possesses these valuable properties in somewhat less degree.

Brunner's method of preparing manganese by means of sodium, does not prevent all fear of the presence of carbon in this metal. The sodium obtained by means of carbonate of soda always contains carbon; the process of Gay-Lussac and Thenard alone furnishes it absolutely pure. Sodium is a very porous metal; charged with naphtha, which often cannot be entirely got rid of on account

* Chem. Gaz., May 1, 1857, p. 163.

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of the slight difference in the density of the two substances, this naphtha always leaves a carbonaceous residue when the sodium is heated. The preparation of a volatile metal, such as magnesium, shows this well, as after its distillation a considerable residue is always found. Lastly, the employment of Hessian crucibles by M. Brunner in presence of sodium, and especially of fluorides, must introduce silicium into a metal so refractory as manganese, if the heat be continued long enough to fuse it. By this process Wöhler has succeeded in causing aluminium to take up 80 to 100 per cent. of silicium, by a quarter of an hour's fusion in contact with fluorides.

In this way perhaps the difference may be explained which exists between the fusing-points of Brunner's manganese, which is liquid at the same temperature as white cast iron, and that described by the author, which is more refractory than iron, as has always been admitted hitherto. Manganese fused in vessels of lime in presence of manganite of lime, decomposes water at a temperature scarcely above the ordinary temperature, as Regnault has observed.

There is, however, one case in which the process with sodium has great advantages, namely, when in the preparation of a refractory simple body it is desired to obtain it crystallized; the sodium* is then caused to react upon the vapour of the chloride when this is volatile, or upon a mixture of the metallic chloride and common salt, and the product of the reduction is heated to a temperature sufficiently high to volatilize the whole or a part of the chlorides. This operation should be performed in crucibles of aluminium. The refractory simple body is then usually found in the crystalline state.

With the sesquichlorides of zirconium, aluminium, or chromium, it is always well to cause the sodium to react upon the double chloride which these substances form with common salt. The double chloride of chromium and sodium is easily obtained by the fusion of the two substances; the chloride of sodium should be in excess, and the chloride of chromium very pure. The crucible is heated to redness before throwing into it the mixture of chlorides and sodium. With the fusible metals, it is well to add a little double chloride of potassium and sodium, as indicated by Wöhler.

At a dull red heat sodium attacks porcelain so energetically, that there is always fear of introducing silicium into the metals prepared in this way. This observation probably explains the difference between the chemical properties of chromium described by the author and M. Fremy. Chromium fused in lime in presence of chromite of lime, and slightly pounded to detach the protective coat of oxide, dissolves very easily in muriatic acid even in the cold, giving a blue solution of Peligot's protochloride of chromium. Bunsen made the same observation on the chromium which he obtained by the pile. Fremy's crystals of chromium, on the contrary, unattacked even by nitromuriatic acid, present a chemical property which may constitute a new and very important case of dimorphism for simple bodies.

* It is often advantageous to replace sodium by aluminium in reductions, as in the preparation of silicium, titanium, zirconium, and boron.

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Dilute sulphuric acid and nitric acid have no action on chromium, as Fremy also found.

In conclusion, the author calls attention to the advantages attending the use of lime crucibles in operating upon metals. M. Debray and himself have found that platinum and its associated metals, treated in small furnaces constructed of lime, come out in a state quite different from that in which they are ordinarily seen, simply because they give up the osmium, and especially the silicium, which they always contain.—*Comptes Rendus*, March 30, 1857, p. 673.

On Leucine and Alanine. By H. Limpricht.

Very recently, by the important investigations of Städeler, Frerichs, Gorup-Besanez, and others, several organic compounds have been discovered to be constant constituents of the animal organism, which were formerly regarded as pathological products, or considered to occur only in a few parts of the body. These discoveries will only acquire their full value in physiology when a clearer light is thrown upon the *constitution* of the compounds. In the present day the labours of chemists are directed rather to the solution of certain theoretical questions than to physiological chemistry, and the investigation of the substances here referred to is frequently attended with peculiar difficulty, from the materials being often difficult to obtain in sufficient quantities. The author therefore wishes the present memoir to be regarded only as a preliminary communication.

Schwanert has decomposed leucine into amylamine and carbonic acid. Dry leucine, heated over the open fire in a small retort, fuses at about 338° F.; and between 363° and 392° F. furnishes an oily fluid, at first colourless but afterwards yellow; in the retort there remains only a small quantity of a brown resinous residue, which is insoluble in water. The distillate possesses a peculiar empyreumatic odour, and at a low temperature solidifies into a mass of soft laminar crystals; it is soluble in water, with the exception of a few oily drops, and also in acids with evolution of carbonic acid; if the solution in muriatic acid be evaporated, large laminar crystals are obtained mixed with a little muriate of ammonia, which remains after treatment with absolute alcohol. The alcoholic solution was evaporated, and agitated with concentrated solution of potash; the fluid separating on the surface, deprived of water by hydrated potash, was distilled with a thermometer immersed in it.

The supposition that this fluid was amylamine was confirmed by the boiling-point, 203° F.; the muriate was prepared, and from this the platinum double salt, which, when dried at 212° F., gave—

	Calculated, $C^{10}H^{13}N, HCl, PtCl^2$.	Found.
Pt	33·6	33·5

This method served to furnish more than an ounce of amylamine from leucine prepared by boiling horn with dilute sulphuric acid.

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Leucine is also produced from proteinaceous substances by fusion with hydrate of potash, and 4 to 5 per cent. of pure amylamine were obtained directly from horn.

About 50 grms. of horn were dissolved by heat in so much solution of potash, that the solution whilst hot was still thickly fluid; and this was carefully distilled to dryness in a glass retort. The distillate, consisting of water, empyreumatic oils, ammonia, &c., was neutralized with muriatic acid, and evaporated to dryness on the water-bath; the residue extracted with strong alcohol, the extract again evaporated, and then distilled with concentrated solution of potash. On the addition of a few fragments of hydrate of potash, the amylamine separated from the distillate.

The dry distillation of alanine furnishes carbonic acid and æthylamine. The experiment was made with 2 grms. of substance, the distillate collected in muriatic acid, brought to dryness, and extracted with absolute alcohol; the precipitate formed by bichloride of platinum in the solution was ignited after drying over sulphuric acid. It gave—

	Calculated, $C^4H^7N, HCl, PtCl^2$.	Found.
Pt	38·5	39·0

There is probably no doubt that glycocoll will furnish methylamine by dry distillation. The author had neither glycocoll nor hippuric acid to try the experiment.

One can hardly venture to attempt the establishment of a rational formula for leucine and its homologues. A body is already known which is decomposed, under the same circumstances, in the same way as leucine and alanine; this is anthranilic or carbanilic acid, which is decomposed at a high temperature into aniline and carbonic acid.

$$\underset{\text{Alanine.}}{C^6H^7NO^4} = \underset{\text{Æthylamine.}}{C^4H^7N} + C^2O^4.$$

$$\underset{\text{Leucine.}}{C^{12}H^{13}NO^4} = \underset{\text{Amylamine.}}{C^{10}H^{13}N} + C^2O^4.$$

$$\underset{\text{Anthranilic acid.}}{C^{14}H^7NO^4} = \underset{\text{Aniline.}}{C^{12}H^7N} + C^2O^4.$$

From this we may assume a similar arrangement of the elements in these compounds, which is also indicated by their reactions, these being to a certain extent similar, although not to the extent that prevails in homologous compounds.

At any rate it remains a remarkable fact, that compounds of the alcoholic radicals amyle and æthyle may be obtained from leucine and alanine, and in such considerable quantity, especially with leucine, which when pure and cautiously heated is almost entirely decomposed into amylamine and carbonic acid, that they cannot be regarded as secondary products of decomposition.

The decomposition of leucine and alanine may be very well explained if we suppose them to contain the radicals amyle and æthyle; but their production from the aldehydes of valerianic and acetic

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acids contradicts this supposition, even if the formation of leucine from thialdine is left out of consideration until it has been confirmed.

But whatever may be the constitution of these compounds, a new way is discovered for the conversion of acids into the alcohols appertaining to them. Piria has discovered that some acids furnish aldehydes by the distillation of their salts with formiates; Strecker has ascertained that the ammonia compounds of these aldehydes are converted into compounds homologous with glycocoll, with hydrocyanic acid, and muriatic acid; this note shows the formation of the amine bases from alanine and leucine, and these furnish the nitrous æther of alcohol and fusel oil by treatment with nitrous acid.—Liebig's *Annalen*, March 1856, ci. p. 295.

On the artificial Formation of Glycerine. *By* A. WURTZ.

In a note on acetal and the glycols, the author put forward the opinion, that the processes adapted to cause the synthesis of the glycols, or diatomic alcohols, ought also to lead to the formation of the glycerines or triatomic alcohols. A glycerine is, in fact, derived from a bromide of carbonated hydrogen, $C^n H^{n-1} Br^3$, by the substitution of an equivalent of oxygen and an equivalent of water for each equivalent of bromine:—

$$C^n H^{n-1} Br^3 = C^n H^{n+2} O^6 + 3HBr.$$

These bromides may be prepared in various ways, and by taking advantage of the powerful affinity of bromine for silver, the above substitution may be effected.

The compound $C^6 H^5 Br^3$ may be prepared in three ways. One of these consists in treating iodide of allyle, $C^6 H^5 I$, or iodized propylene of Berthelot, with bromine. The iodized liquid is placed in a long-necked flask, surrounded by a refrigerating mixture, and one and a half times its weight of bromine is added in small quantities. The iodine separates in a crystalline form, whilst 3 equivs. of bromine are fixed upon the group $C^6 H^5$.

The tribromide thus obtained, when properly purified, forms a dense colourless liquid, which is slightly rose-coloured if it retains a trace of iodine. At a temperature below 50° F. it crystallizes in fine colourless prisms, which fuse at 61° F. It distils unaltered at 422°–423° F. 205 grms. of acetate of silver were treated with 115 grms. of this tribromide, dissolved in 5 or 6 times its volume of crystallizable acetic acid. The paste thus formed was heated for eight days on the oil-bath to a temperature of 248°–257° F. On the conclusion of the reaction, the contents of the flask were thrown upon a filter, and the bromide of silver washed with æther.

The liquid was distilled until the thermometer marked 284° F.; the residue was treated with lime and æther. The colourless ætherial solution, when evaporated on the water-bath, left 15·5 grms. of a neutral yellowish oil. This was distilled, when a few drops only passed at 482° F., and the greater part of the liquid passed at 532° F. The perfectly colourless product is neutral, possesses a

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slight odour of acetic acid, and is heavier than water, at the bottom of which it forms an oily stratum. When agitated with a great excess of water, it dissolves. It is soluble in all proportions in alcohol and æther. It contains—

	Found.	$C^{18} H^{14} O^{12}$.
C	49·12	49·5
H	6·60	6·4

The formula $C^{18} H^{14} O^{12}$ is that of triacetine. The product analysed really contained 3 equivs. of acetic acid and 1 equiv. of glycerine. 0·647 gr. of the artificial triacetine were saponified by baryta-water. The liquid was freed from the excess of baryta by a current of carbonic acid and distillation, and precipitated by sulphuric acid. 0·974 gr. of sulphate of baryta was obtained, representing 2·8 or 3 equivs. of acetic acid.

To obtain artificial glycerine, triacetine was saponified by baryta-water, and the liquid freed from the excess of baryta was evaporated to dryness. The residue was treated with absolute alcohol containing a small quantity of æther. The liquid, evaporated on the water-bath, left glycerine, which was evaporated *in vacuo*. At about 392° F. a very thick colourless liquid, of a distinctly saccharine taste, passed; it was soluble in all proportions in water and alcohol, but insoluble in æther. This liquid gave on analysis C 38·5, H 8·6. The formula $C^6 H^8 O^6$ requires C 39·1, H 8·6. To verify its identity with glycerine, it was treated with iodide of phosphorus, PI^2; a very brisk reaction took place, and iodized propylene was obtained.

The tribromide, $C^6 H^5 Br^3$, fusible at 61° F., and boiling at 422° to 423° F., is not identical with tribromhydrine. According to Berthelot's experiments, this is a colourless liquid, fuming slightly in the air, and distilling at about 356° F. But if the solid tribromide gives a glyceric compound by reacting upon acetate of silver, this must be attributed to a molecular alteration taking place at the moment of the reaction.—*Comptes Rendus*, April 13, 1857, p. 778.

On Bimethylamine and some of its Compounds. By T. Petersen.

If we glance at the mode of formation of tricapronylamine*, it is easy to see that 3 atoms of œnanthylic aldehyde furnished the base, carbonic acid and water by the reception of oxygen and 1 atom of ammonia. This phænomenon of decomposition must therefore be exceedingly interesting, although under similar circumstances other aldehydes of the series of fatty acids furnished volatile bases containing a radical one grade lower. From the acid sulphite of aldehyde-ammonia Gössmann obtained a volatile amine base, the muriate of which possessed the composition of muriate of æthylamine. Bimethylamine,

$$\left.\begin{matrix} C^2 H^3 \\ C^2 H^3 \\ H \end{matrix}\right\} N,$$

is metameric with æthylamine; consequently an explanation of the

* See Chem. Gaz., May 15, 1857, p. 183.

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formula could only be furnished by substitution in the way described by Hofmann, by means of the iodide of an alcohol radical. The compound in question has now actually proved to be bimethylamine. The preparation of the base was effected in the mode described by Gössmann. Acid sulphite of aldehyde-ammonia was mixed with four times its quantity of a mixture of caustic lime and hydrated lime, and heated in a retort. The gas evolved was passed into dilute muriatic acid, the solution evaporated to dryness in the water-bath, and the muriate of the base extracted from the mass of muriates of ammonia and base by means of anhydrous alcohol and æther.

The compound was also obtained by heating acid sulphite of aldehyde-ammonia by itself. When the dry salt is heated to 248° F. in a sealed glass tube, the mass becomes yellow; and if the temperature be raised to 284° F., it is completely changed. On opening the tube, sulphurous acid is recognized by its odour, sulphur has been deposited, and acicular crystals of a sulphate are attached to the walls of the tube. When the mass had been dissolved in water, and the sulphur separated by filtration, muriatic acid was added to the fluid; this evolved carbonic acid and some sulphuretted hydrogen, and the odour of aldehyde was recognizable on the application of heat. With perchloride of iron considerable quantities of acetic acid were detected. An excess of potash evolved ammonia, and therewith unmistakeably an amine base. The fluid was then mixed with alkali in a retort, and the gas evolved absorbed by dilute muriatic acid. The retort was gently heated. After concentration, the solution in muriatic acid was precipitated by perchloride of platinum; the precipitate, which resembled platinochloride of ammonium, was filtered, washed, and dried. The amount of platinum in this salt must give the proportion of platinochloride of ammonium to the platinum double salts of the amine bases. The quantity of the separated sulphur and that of the sulphuric acid formed were also determined. It appeared that from 9 atoms of sulphurous acid, about 1 atom of sulphur, 6 atoms of sulphurous acid, and 2 atoms of sulphuric acid were obtained.

The platinum-salt, after ignition, left 42·786 per cent. of platinum. Platinochloride of ammonium contains 44·2 per cent. of platinum; platinochloride of bimethylamine, 39·3 per cent. The salt contained therefore about two-thirds platinochloride of ammonium.

With regard to the deposition of sulphur, it must also be observed that acid sulphite of ammonia gradually deposits sulphur when the air is excluded. When this salt had been heated for some time in the oil-bath to 284° F., a great part of the sulphurous acid was decomposed into sulphur and sulphuric acid.

The mixture of muriates of ammonia and of the base obtained in the way described, was again extracted by a mixture of absolute alcohol and æther, and the salt obtained by evaporation again treated therewith, in order to obtain a compound quite free from muriate of ammonia. As the salt obtained by both methods exhibited the same properties, a mixture of the two was made use of to effect the substitution experiment.

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Protiodide of Bimethylbiæthylammonium, C^2H^3, C^2H^3, C^4H^5, C^4H^5, N, I.—Muriate of bimethylamine was mixed with a little water in a small digesting glass, and a conducting tube was attached, opening into a small tube with iodide of æthyle; for the purpose of drying the gas afterwards set free, a tube filled with fragments of hydrate of potash was also attached. A few fragments of hydrate of potash were thrown into the digesting glass, and a gentle heat was applied to it. The reaction was violent, and a gas of a strong ammoniacal odour was evolved, and rapidly absorbed by the iodide of æthyle. After the completion of the decomposition, the tube was sealed up, and heated for a long time in the water-bath to 212° F. The fluid contained in it had then acquired a reddish colour, and was filled with white tabular crystals of the present compound. They are readily soluble in water and alcohol.

Protochloride of Bimethylbiæthylammonium and Bichloride of Platinum, C^2H^3, C^2H^3, C^4H^5, C^4H^5, NCl, $PtCl^2$.—The excess of iodide of æthyle was separated from the preceding compound by distillation on the water-bath, and the thick, partially syrupous brown residue dissolved in water. The iodides of the ammonium bases usually acquire this form by this mode of treatment. The solution was then gently heated for some time with hydrated oxide of silver, and the iodide of silver and excess of oxide of silver separated by filtration. The fluid had an alkaline reaction, and had dissolved some oxide of silver, which was removed by muriatic acid, by which the hydrated oxide of bimethylbiæthylammonium produced by the removal of the iodine was converted into the chloride. On the addition of bichloride of platinum to the dilute solution, only a turbidity was produced; but after concentration on the water-bath, columnar and tabular crystals of the platinum double salt separated. They were of a slightly yellow colour, but nearly limpid; tolerably soluble in water, but more difficult of solution in alcohol and æther, and became yellow and opake by exposure to the air. Bichloride of platinum produces a thick orange-yellow precipitate in concentrated solutions. The analysis of the salt, dried at 212° F., gave—

C	23·43	12	23·43
H	5·31	16	5·22
N	..	1	4·55
Cl	..	3	34·67
Pt	32·28	1	32·13

Bimethylamine has not yet been prepared in a state of purity. Even Hofmann, who first worked out the amine bases, did not detect this compound. If ammonia be allowed to react upon protochloride of methyle, with certain quantitative proportions bimethylamine may certainly be produced; but as in this reaction other decompositions, which cannot always be exactly determined beforehand, occur, the correct proportions can hardly be attained when we have to do with the preparation of an amine base, which possesses such a constitution as bimethylamine. If we have methylamine and bimethylamine or bimethylamine and trimethylamine together, the exact

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separation of their salts in small portions would probably be impossible.

Bimethylamine is combustible, possesses an extremely strong ammoniacal odour, and is gaseous at ordinary temperatures. When the muriate was decomposed by potash in a small retort, and the gas evolved, after passing through a drying tube filled with fragments of potash, was passed through the tube of evolution to the bottom of a long tube, cooled by a mixture of common salt and snow to $-2°$ F., some oily drops were condensed. When the glass tube was but slightly raised out of the freezing mixture, a rapid volatilization of the body took place. Bimethylamine therefore appears to boil many degrees below 32° F.

Muriate of Bimethylamine, $C^2 H^3$, $C^2 H^3$, H, N, HCl.—This salt, prepared in the way already described, forms white, laminar, crystalline masses, which are very hygrometric and readily fusible. It dissolves in water, and also without difficulty in alcohol, but is far less soluble in æther.

Muriate of Bimethylamine and Bichloride of Platinum, $C^2 H^3$, $C^2 H^3$, H, N, HCl, $PtCl^2$.—Bichloride of platinum produces a yellow precipitate in solutions of muriate of bimethylamine; this is rather difficult of solution in water, and is still less soluble in alcohol and æther. The analysis of the salt, dried at 212° F., gave 39·63 and 39·34 per cent. of platinum. Calculated, 39·31.

The decomposition by bisulphite of ammonia of two aldehyde compounds belonging to members of the fatty acid series which are tolerably wide apart, was therefore perfectly concordant. It is true, one of the bases obtained is a nitrile base and the other an imide base; but in each case a volatile base was formed from the aldehyde and ammonia, in which the alcohol radical of the next lower fatty acid group was detected. We may therefore be almost certainly convinced that other aldehydes of the same series will behave similarly.

Mitscherlich regarded the fatty acids as compounds of oxalic acid with hydrocarbons. The phænomena of their decomposition may perhaps be explained in accordance with this. According to Gerhardt, the fatty acids are formic acids, in which 1 atom of hydrogen is replaced by a hydrocarbon. By this mode of looking at the subject, therefore, it may be said that carbonic acid and methyle are produced from aldehyde or formylmethyle, and carbonic acid and capronyle from œnanthole.—From the author's *Inaugural Dissertation*, Göttingen, 1857.

On a new Mode of Formation of Protoxide of Silver.
By Prof. WÖHLER.

The yellow arsenite of silver becomes black when heated either by itself or with solution of potash. The author thought, from the behaviour of arsenite of copper, which is converted by solution of potash into red protoxide of copper, that a similar change might take place here, and he has found this to be the case.

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If the yellow arsenite of silver be poured over with a concentrated solution of soda and heated, it rapidly becomes black. To complete the action, it must be kept boiling for a considerable time; and the fluid must be poured away from the black powder, which settles readily, and replaced by fresh solution of soda. If this be neglected, it retains arsenic. It is then well washed and dried, when it forms a heavy black powder with a tinge of gray. Under the burnisher it acquires a dull metallic lustre.

The soda solution contains *arseniate* of soda, which sometimes even crystallizes from it. If the arsenic acid be thrown down by magnesia salt and ammonia, no arsenious acid is found in the filtered fluid.

The black body is a mixture of silver and protoxide of silver, in equal equivalents, formed by two-thirds of the oxygen of the oxide of silver in 1 equiv. of $3AgO\ AsO^3$, converting the arsenious acid into arsenic acid $= Ag^2O + Ag + AsO^5$.

When heated alone, it readily becomes converted into grayish-white metallic silver, with a loss of 2·4 per cent. of oxygen. Pure protoxide of silver would lose 3·56 per cent. When muriatic acid is poured over it, it becomes somewhat grayer, and changes its appearance in general; it is converted into a mixture of silver and chloride of silver, the latter extractible by ammonia. Hydrocyanic acid behaves similarly. In nitric acid it dissolves readily to form a persalt, with evolution of nitrous oxide gas.

When arsenite of silver is heated alone in a glass tube, it becomes black at a certain temperature. With a somewhat stronger heat, arsenious acid sublimes. Ammonia then extracts *arseniate* of silver, leaving metallic silver; the arseniate may be precipitated by nitric acid, with its peculiar reddish-brown colour. Hence it appears that 2 atoms of arsenite of silver are decomposed into 1 atom of arseniate of silver, 1 atom of protoxide of silver, 1 atom of silver, and 1 atom of arsenious acid.

As common arsenious acid was employed in the preparation of the arsenite of silver, the product contained antimony, although the acid was dissolved in ammonia. When the black protoxide obtained by treatment with solution of soda was calcined and the silver dissolved in nitric acid, white antimoniate of silver remained undissolved. To obtain the silver-salt free from antimony, a solution of arsenious acid in ammonia was boiled until most of the ammonia was volatilized, and a great part of the acid separated. The solution was then mixed with an excess of nitrate of silver, the slight yellowish-white antimonial precipitate separated by filtration, and the solution then carefully precipitated by ammonia. The bright yellow precipitate is flocculent at first, but soon collapses into a heavy yellow powder, especially when heated.

The author confirms Hirzel's observation, that after all the arsenite of ammonia has been crystallized from a solution of arsenious acid in ammonia, very large crystals of arsenious acid, free from ammonia, and of a very unusual appearance, are deposited in it by spontaneous evaporation. They form rose-like aggregations of

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tabular crystals of a very vivid nacreous lustre. They evidently consist of segments of regular octahedra, similar to the tabular crystals of alum.—Liebig's *Annalen*, March 1857, ci. p. 363.

On some Derivatives of Naphthylamine. *By* HUGO SCHIFF.

Amongst the organic bases which have not yet been closely studied, naphthylamine, first prepared by Zinin, is especially deserving of a more exact investigation.

The method recently described by Béchamp, for preparing the amide bases from their nitro-compounds by means of iron and acetic acid, in accordance with the general formula,

$$\text{Base}\left\{\begin{matrix}-\text{H}\\+\text{NO}^4\end{matrix}\right\}+4\text{Fe}+6\text{C}^4\text{H}^4\text{O}^4=\text{Base}\left\{\begin{matrix}-\text{H}\\+\text{NH}^2\end{matrix}\right\}+6\text{C}^4\text{H}^3\text{feO}^4+4\text{HO}^*$$

induced the author to prepare a large quantity of this body, and to investigate its behaviour towards various reagents more closely.

For preparing this, nitronaphthaline, $\text{C}^{20}\text{H}^7\text{NO}^4$ (which for this purpose should not be recrystallized from alcohol, but only freed from adherent nitric acid by washing with water), was most intimately mixed with the corresponding quantity of iron filings in a mortar, and mixed with dilute acetic acid to the consistence of a paste, in a retort capable of holding ten times the quantity. The reaction soon commences of itself, but it may be assisted by a very gentle heat. As soon as it begins, the heat is removed, and the neck of the retort is turned upwards, in order that the strongly inflated mixture may not contaminate the neck. After the reaction is completed, the excess of acetic acid, which always contains some dissolved naphthylamine, is distilled off, the retort is allowed to cool, and tolerably concentrated solution of potash is added. It is best now to leave it standing for some hours, in order that the mass may be completely penetrated by the solution of potash, and the whole belly of the retort is then surrounded with live coals, when the naphthylamine which has been set free begins to distil over at 572° F.; it is collected in a well-cooled receiver, in which it is advisable to put a little concentrated acetic acid, in order that the vapours of naphthylamine passing over may be at once fixed thereby. When nothing more passes, the contents of the receiver are repeatedly extracted with dilute acetic acid (as some undecomposed nitronaphthaline always passes over), and filtered; the naphthylamine is precipitated from the distillate by potash. In this way it is obtained in the form of white flakes, which give a milky turbidity to the fluid, and only become converted into long needles after standing quietly for several hours. These needles, like all salts of naphthylamine, acquire a yellow colour when exposed to the light and in contact with the air; they afterwards become red, and finally brown. When heated cautiously and gradually,

* The author adopts Gerhardt's views, according to which $\text{fe}=\frac{3}{2}\text{Fe}=18{\cdot}66$.

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naphthylamine may be sublimed; it is then obtained in long silky needles, which only become coloured when they are left for a long time in the air or in the sunlight. The compound has the empirical formula $C^{20} H^9 N$, and the rational formula $N\left\{\begin{matrix} C^{20} H^7 \\ H \\ H \end{matrix}\right.$. The naphthylamine obtained in this way was then employed in the preparation of the following bodies.

Æthylonaphthylamine.—A small flask, containing a mixture of purified naphthylamine and an excess of bromide of æthyle, is fixed to the inferior extremity of a Liebig's refrigeratory apparatus, in such a way that all the vapours condensing in the tube must flow back into the vessel. The temperature is kept at about 104° to 122° F., the boiling-point of bromide of æthyle. In a few hours the contents have become converted into a reddish-brown mass, from which the excess of bromide of æthyle is distilled away, and the mass is then repeatedly extracted with boiling water. On the cooling of the extracts, which are filtered whilst hot, the bromide of the new base separates in concentrically-grouped small needles, and these can be obtained of a pale rose colour by recrystallization. A perfectly white compound could not be prepared; but this slight coloration, which is rarely to be avoided in organic compounds, does not appear to have any great influence upon the result of the analysis.

If naphthylamine be enclosed in a glass tube with bromide of æthyle, and left to stand quietly at the ordinary temperature of the room for some days, a few crystals make their appearance, and in about a fortnight the whole tube is nearly filled with crystals of the bromide.

Bromide of Æthylonaphthylammonium, the formation of which is easily explained by the equation

$$N\left\{\begin{matrix} C^{20} H^7 \\ H^2 \end{matrix}\right. + \left.\begin{matrix} C^4 H^5 \\ Br \end{matrix}\right\} = N\left\{\begin{matrix} C^{20} H^7 \\ C^4 H^5 \\ H^2 \end{matrix}\right\} Br,$$

is very slightly soluble in cold water; in hot water, alcohol and æther it dissolves pretty easily, and may be obtained therefrom crystallized in small needles. It does not become coloured so easily as naphthylamine. The compound contains 31·55 per cent. or 1 equiv. of bromine.

Iodide of Æthylonaphthylammonium, $C^{24} H^{14} NI$, was obtained from naphthylamine and iodide of æthyle. It much resembles the bromide in its solubility, but is much more easily decomposable. It crystallizes in shining four-sided prisms. It contains 42·32 per cent., or 1 equiv. of iodine.

With solution of potash a solution of the bromide gave a white caseous precipitate, which in course of time formed needles, and soon acquired colour. To ascertain whether this was the separated imide base, æthylonaphthylamine, the following experiments were made.

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A portion of the precipitate was dissolved in hot dilute muriatic acid. On cooling, reddish silky needles were obtained; these were soluble in water, and more easily in alcohol and æther. Two determinations of the chlorine were made; they gave 19·3 and 19·5 per cent. of chlorine. These amounts of chlorine do not correspond with chloride of æthylonaphthylammonium, which would require 16·9 per cent., but with chloride of naphthylammonium, as appears from the following analysis:—

C	..	..	20 =	120	66·88
H	..	..	10	10	5·57
N	..	..	1	14	7·78
Cl	19·3	19·5	1	35·5	19·77

A further portion of the precipitate was treated with bromide of æthyle in the way already described, and the mass obtained extracted with hot water. Peach-red, spherically-grouped needles were obtained, containing 31·72 per cent. of bromine.

This agrees with bromide of æthylonaphthylammonium. Bromide of diæthylonaphthylammonium, which would probably have been produced by the action of bromide of æthyle upon æthylonaphthylamine, would require 28·5 per cent. of bromine.

From these experiments it follows that the precipitate obtained with potash is nothing but naphthylamine, and therefore that the base is not separable by potash from the salts of æthylonaphthylamine. The equation

$$N\left\{\begin{matrix}C^{20}H^{7}\\C^{4}H^{5}\\H^{2}\end{matrix}\right\}Br+\left.\begin{matrix}Ka\\H\end{matrix}\right\}O^{2}=N\left\{\begin{matrix}C^{20}H^{7}\\H^{2}\end{matrix}+\begin{matrix}C^{4}H^{5}\\H\end{matrix}\right\}O^{2}+\left.\begin{matrix}Ka\\Br\end{matrix}\right\}$$

may perhaps furnish an expression for the decomposition which takes place in this case.

Experiments with the view of preparing salts of æthylonaphthylamine from bromide of æthylonaphthylammonium led to no result.

By the treatment of naphthylamine with iodide of methyle, in order to prepare an iodide of methylonaphthylammonium, a greasy mass was obtained, which would not crystallize from water, alcohol, or æther, and the further investigation of which had to be given up. An attempt to prepare phenylonaphthylamine from naphthylamine and aniline, in which 1 equiv. of ammonia would have had to be eliminated, also gave a negative result. No action occurred, either by heating in a sealed tube in the oil-bath, or by distillation in a retort. The aniline distilled off unchanged.

Naphthylurea.—An attempt was made, in the same way as for the formation of ordinary urea from sulphate of ammonia and cyanate of potash, to prepare a urea in which 1 equiv. of hydrogen would be replaced by the atomic group $C^{20}H^{7}$, naphthyle, or a urea of the formula $C^{2}\left\{\begin{matrix}C^{20}H^{7}\\H^{3}\end{matrix}\right\}N^{2}O^{2}$. This could not be effected in this way.

The desired urea was, however, obtained in another manner. A solution of naphthylamine in anhydrous æther was saturated with gaseous cyanic acid (prepared by heating cyanuric acid), and the

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solution was left to spontaneous evaporation. Shining laminæ were obtained, which were insoluble in water and alkalies, and decomposed by acids. Their solution in alcohol, heated for some time and then evaporated at a gentle heat, deposited flat, shining, flexible needles. These were scarcely soluble in water, sparingly in æther, but very easily in alcohol. A concentrated alcoholic solution of them gave a crystalline compound with concentrated solution of oxalic acid. A solution mixed with nitric acid was decomposed with evolution of gas, and at the same time the fluid became blood-red. Notwithstanding repeated recrystallizations, the substance could only be obtained of a yellow colour, so that it would almost appear as if this was its proper colour. The analysis gave—

C	70·75	22 =	132	70·96
H	5·45	10	10	5·38
N	14·35	2	28	15·05
O	9·45	2	16	8·61

Should Natanson's experiments, which appear to prove the identity of urea and carbamide, receive confirmation, ordinary urea would have the rational formula $N^2\left\{\begin{matrix}C^2O^2\\H^2\\H^2\end{matrix}\right.$, and consequently naphthylurea would be $N^2\left\{\begin{matrix}C^2O^2\\H\,.\,C^{20}H^7\\H^2\end{matrix}\right.$. The dinaphthylocarbamide prepared by Delbos would then be a urea with 2 equivs. of hydrogen replaced by naphthyle. It deserves to be remarked, that ordinary urea behaves exactly like an amide of carbonic acid towards water at a high temperature, or when boiled with acids or alkalies, as well as under the action of deamidizing agents, such as nitrous acid or chlorine.

Bromide of Naphthylammonium, $C^{20}H^{10}NBr$.—If a concentrated alcoholic solution of sulphate of naphthylamine be mixed with an equivalent quantity of a concentrated solution of bromide of potassium or barium, a crystalline precipitate is deposited after the lapse of a short time in the former case, and immediately in the latter; this consists of the sulphate of the base which had been combined with the bromine. When the coloured solution is slowly evaporated, it leaves a crystalline residue, which is easily soluble in alcohol, but less so in cold water. The body gave 35·53 per cent. of bromine; the above formula requires 35·73 per cent.

The mode of formation of this salt by double decomposition is explained by the equation

$$S^2\left\{\begin{matrix}C^{20}H^{10}N\\H\end{matrix}\right\}O^8+KaBr=N\left\{\begin{matrix}C^{20}H^7\\H^3\end{matrix}\right\}Br+S^2(KaH)O^8.$$

Iodide of Naphthylammonium.—Sulphate of naphthylamine, mixed with a solution of iodide of potassium, gave a precipitate of sulphate of potash. The alcoholic solution left a resinous mass. It gave the reaction of iodine, and burnt without residue. It was decomposed even by the attempt to dissolve it in hot water.

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Nitronaphthylamine was obtained by Laurent as a red substance, by treating binitronaphthaline with sulphuretted hydrogen.

If naphthylamine be added in small portions to nitrosulphuric acid, a strong reaction occurs, the mixture becoming very dark green. When this is diluted with water, yellowish-red flakes separate; these are probably nitronaphthylamine. They are insoluble in water and muriatic acid; they dissolve with a red colour in alcohol, sulphuric acid, nitric acid, and potash, and by the addition of water to these solutions, they are again separated, as also from the solution in potash, by neutralization.

With iron and acetic acid they furnish brown flakes of a base, the reactions and solubilities of which agree with those of the azonaphthylamine $N^2\left\{\begin{matrix}C^{20}H^6\\H^4\end{matrix}\right.$ prepared by Zinin.

The recent discovery of Wurtz in the preparation of glycolic alcohol, that with the diminution of hydrogen the radicals unite an increase of basicity, gives us an explanation of a great number of phænomena. Thus, for example, in regard to the constitution of the semi-amines (azo-amines, *Gerhardt*), it appears from the following that the equivalent bodies are—

	1 H.	2 H.
In the æthyle group	C^4H^5, æthyle	C^4H^4, æthylene.
In the propyle group	C^6H^7, propyle	C^6H^6, propylene.
In the phenyle group	$C^{12}H^5$, phenyle	$C^{12}H^4$, phenylene.
In the naphthyle group	$C^{20}H^7$, naphthyle	$C^{20}H^6$, naphthylene.

Phenylamine and naphthylamine then contain the monobasic, and azophenylamine (semibenzidam) and azonaphthylamine the bibasic radicals. These are derived from—

	NH^3.	N^2H^6.
In the phenyle group	$N\left\{\begin{matrix}C^{12}H^5\\H^2\end{matrix}\right.$, aniline	$N^2\left\{\begin{matrix}C^{12}H^4\\H^4\end{matrix}\right.$, azophenylamine.
In the naphthyle group	$N\left\{\begin{matrix}C^{20}H^7\\H^2\end{matrix}\right.$, naphthylamine	$N^2\left\{\begin{matrix}C^{20}H^6\\H^4\end{matrix}\right.$, azonaphthylamine.

Lastly, we also get an explanation why the biaminic acids of the monobasic acids are destitute of the acid character. As will be shown hereafter, the aminic acids of the monobasic acids correspond with the type $\left.\begin{matrix}NH^4\\H\end{matrix}\right\}O^2$; they therefore still possess a displaceable equivalent of hydrogen. But in the biaminic acids this is also displaced by the type NH^4, so that they correspond with the fundamental form $\left.\begin{matrix}NH^4\\NH^4\end{matrix}\right\}O^2$, and hence it arises that these so-called acids possess no acid, but only basic properties. The aminic acids contain the monobasic, and the biaminic acids the bibasic radical, as may be seen for example in the case of benzoic acid.

Benzoic acid,

(Phenyloformic acid) $\left.\begin{matrix}C^2(C^{12}H^5)O^2\\H\end{matrix}\right\}O^2$ corresponds with $\left.\begin{matrix}H\\H\end{matrix}\right\}O^2$,

and contains $C^{12}H^5=1H$.

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Benzaminic acid,

(Phenylocarbaminic acid) $\left.\begin{matrix}NH.C^{12}H^5.C^2O^2\\H\end{matrix}\right\}O^2$ corr. with $\left.\begin{matrix}NH^4\\H\end{matrix}\right\}O^2$,

saturates bases, and contains $C^{12}H^5=1H$.

Bibenzaminic acid,

(Oxide of phenylenocarbammonium) $N^2\left\{\begin{matrix}C^2O^2\\C^{12}H^4\\H^4\end{matrix}\right\}O^2$ corr. with $\left.\begin{matrix}NH^4\\NH^4\end{matrix}\right\}O^2$,

saturates acids, and contains $C^{12}H^4=2H$.

Voit did not succeed in combining bibenzaminic acid with bases. He only obtained compounds in which the so-called acid played the part of a base, and saturated 2 equivs. of acid. The bibasic oxyphenic acid, $\left.\begin{matrix}C^{12}H^4\\H^2\end{matrix}\right\}O^4$, appears to be the phenylenic alcohol analogous to glycolic alcohol.

Colour Reactions of Naphthylamine and Oxynaphthylamine.—The above-mentioned nitrogen determination of naphthylurea does not agree sufficiently well with the calculation. This determination of nitrogen was effected with a measured quantity of sulphuric acid of known strength. When, after the completion of combustion, a normal solution of soda was added to the fluid reddened with litmus, the latter constantly became redder, and at last purple-red, so that the alkaline reaction had to be ascertained with litmus-paper. It is probable that too much solution of soda was added, from which the difference in the analysis may arise. A second case, standing in connexion with this, occurred to the author with the portion of naphthylurea, the preparation of which was not successful. The æther might perhaps have still contained some water, so that the cyanic acid passed in was decomposed. On evaporating the red ætherial solution, there remained a purple syrupous mass, which was coloured violet by acids, whilst alkalies reproduced the red colour. By soaking blotting-paper with the alcoholic solution, a test-paper was obtained, which presented exactly the opposite reactions to litmus-paper. Should not these colour reactions stand in some near connexion with the relationship of the naphthaline compounds to the colouring matter of madder? Sacc has already observed, that paper coloured with tincture of madder is rendered violet by acids and yellow by alkalies. It is well known that the red colour of madder is considerably heightened by alkalies, and that this red colour acquires a bluish tinge with acids.

A body which exhibits the above colour reactions, and which may be obtained crystallized, was procured by Church and Perkins by the treatment of naphthylamine with nitrous acid. Its composition is $C^{20}H^8(NO^2)N$. Other observers have also made us acquainted with coloured derivatives of naphthylamine. Thus by heating naphthaline with chromate of potash and sulphuric acid, Laurent is said to have obtained a substance of a beautiful carmine-red colour, carminnaphtha. Laurent also mentions a substance which is to be obtained by the dry distillation of nitronaphthaline

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with lime or baryta, and which he calls naphthase. A small quantity of this is said to be sufficient to give a violet colour to a large quantity of sulphuric acid. The author has not succeeded in obtaining these substances.

Dusart, who studied the action of potash-lime upon nitronaphthaline, also obtained by this means a series of compounds possessing colour reactions.

Oxynaphthylamine.—When Piria mixed the solution of a salt of naphthylamine with perchloride of iron or gold, or with nitrate of silver, he obtained an indigo-blue precipitate, to which he gave the name of naphthameine. He states that naphthylamine, in passing into this new body, loses the elements of hydrogen and ammonia. In the analyses which the author undertook with substances from various preparations, it appeared that this body is by no means oxidized naphthylamine minus the elements of ammonium, but that it rather contains carbon, hydrogen, and nitrogen, in the same equivalent proportions as naphthylamine, of which it is only a simple product of oxidation. The author therefore proposes for it the name of *oxynaphthylamine.* A relation such as that between orcine and orceine, to which perhaps the name naphthameine is intended to refer, does not exist.

A similar precipitate could also be produced with the perchlorides of platinum, zinc, tin, and mercury, and with chromic acid. It is probable that the violet colour, which naphthylamine acquires by long keeping, is also due to the formation of this product of oxidation. The author found its solubility the same as described by Piria. In the moist state it possesses a peculiar odour, similar to that of iodine, which becomes stronger when the compound is heated. It cannot be sublimed; when heated, it burns, leaving a coal which is difficult of combustion. Sulphurous acid produces no alteration in it. In moist air or under water it very soon loses its blue colour and becomes violet, so that it is difficult to obtain this compound of a pure blue colour in the dry state. After precipitation by means of the metallic chlorides, neither chlorine nor metal could be detected in the compound. In precipitation with gold, silver, or mercury, the metals are very quickly reduced. Compounds of this body with acids or bases could not be prepared, nor could it be obtained crystallized.

The substance employed for the analyses was obtained in the following ways:—1st, by precipitation from a neutral solution of chloride of naphthylammonium by perchloride of iron; 2ndly, by precipitation from a solution of the sulphate by chromic acid; 3rdly, prepared in the same way, and thrown down by water from the solution in concentrated sulphuric acid; 4thly, by precipitation from the solution of the acetate by chromic acid. The following numbers were obtained, all agreeing with the formula $C^{20} H^{9} NO^{2}$:—

C	74·09	75·41	75·34	20	120	75·47
H	5·70	5·71	5·39	9	9	5·66
N	8·75	8·93	..	1	14	8·80
O	..	..	..	2	16	10·07

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The mode of formation of this product of oxidation may be understood from the formulæ,—

$$3(S^2 \begin{matrix} C^{20} H^{10} N \\ H \end{matrix} O^8) + 4CrO^3 = 3C^{20} H^9 NO^2 + 3S^4 cr^2 O^8 + 6HO.$$

$$C^{20} H^{10} NCl + 6feCl + 2HO = C^{20} H^9 NO^2 + 4FeCl + 3HCl.$$

Naphthylamine and Sulphuret of Carbon.—An imide of carbonic acid and sulphocarbonic acid, derived from the type NH^3, such as we are acquainted with for other bibasic acids, has not yet been prepared, any more than derivatives therefrom; the author therefore wished to try whether by bringing in contact anhydrous sulphocarbonic acid and naphthylamine, nearly in accordance with the equation $N\left\{\begin{matrix} C^{20} H^7 \\ H^2 \end{matrix}\right\} + C^2 S^4 = N\left\{\begin{matrix} C^2 S^2 \\ C^{20} H^7 \end{matrix}\right\} + 2HS$, a naphthylosulphocarbimide was to be obtained, and from this naphthylocarbimide. For this purpose sulphuret of carbon was enclosed in a glass tube with naphthylamine, and heated to 212° F. At the commencement, the contents of the tube dissolved into a dark red fluid; after boiling for several hours, however, the whole became a solid mass. On opening the tube, a violent evolution of sulphuretted hydrogen took place. The mass was pressed between bibulous paper, and as it was found to be insoluble in cold æther and alcohol, it was washed with both these fluids until they ran away from the white mass without being rendered turbid. The compound, consisting of small interlaced needles, was finally placed over sulphuric acid, by which means the last portions of naphthylamine passed over into the acid.

To ascertain whether the fluid was the required naphthylosulphocarbimide, the sulphur was determined, and found to be 9·81 per cent. From this it follows that the compound analysed was not naphthylosulphocarbimide, which requires 17·3 per cent. of sulphur, but that it was rather dinaphthylosulphocarbamide.

During the reaction, therefore, 2 equivs. of naphthylamine had been active, and the change had taken place in accordance with the equation

$$2N\left\{\begin{matrix} C^{20} H^7 \\ H^2 \end{matrix}\right\} + C^2 S^4 = N^2\left\{\begin{matrix} C^2 S^2 \\ (C^{20} H^7)^2 \\ H^2 \end{matrix}\right\} + 2HS.$$

Dinaphthylosulphocarbamide has already been prepared by Delbos.

Trinaphthylophosphamide.—If naphthylamine be heated on the water-bath with oxychloride of phosphorus, a non-crystalline reddish product is obtained, whilst the excess of fluid contains dissolved chloride of naphthylammonium. The dried substance is pretty readily decomposable in hot water, and also by boiling with alkalies or acids. The solutions contain naphthylamine and phosphoric acid. During fusion with potash, naphthylamine is evolved, and phosphate of potash is obtained. As the author has ascertained that triphosphamide, $N^3\left\{\begin{matrix} PO^2 \\ H^6 \end{matrix}\right.$, is produced from oxychloride of phosphorus and ammonia, and triphenylophosphamide, $N^3 PO^2 (C^{12} H^5)^3 H^3$, from

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the former substance and aniline, the substance in question is undoubtedly, according to the equation

$$PO^2Cl^3 + 6C^{20}H^9N = N^3PO^2(C^{20}H^7)^3H^3 + 3NC^{20}H^{10}Cl,$$

the corresponding trinaphthylophosphamide.—From the *Author's Inaugural Dissertation*, Göttingen, 1856; *Chemisches Centralblatt*, No. 11, March 18, 1857, p. 166.

On the Preparation of Æthylamine from Urea. *By* D. K. Tuttle.

With the view of finding a method by which æthylamine may be prepared more easily, and in larger quantities than hitherto, the author has made a series of experiments, some of which led to a process by which considerable quantities of æthylamine may be obtained from easily accessible materials.

Cyanate of potash was first prepared from ferrocyanide of potassium. The crude mass was mixed with sulphovinate of lime and hydrate of lime, and the mixture heated in a retort, the receiver of which contained muriatic acid. The contents of the receiver were evaporated to dryness, and the residue extracted with a mixture of alcohol and æther to separate the muriate of ammonia. The solution furnished a deliquescent salt. This was treated with an alkali; the gas evolved was dried by caustic potash, and condensed by a freezing mixture. In this way a fluid was obtained possessing all the properties of æthylamine.

The best results were obtained by heating a mixture of urea, caustic lime, and sulphovinate of lime. Urea was mixed with about 5 parts of sulphovinate of lime and an excess of caustic lime; the mixture was heated in a retort, with muriatic acid in the receiver. The residue of the contents of the receiver, after the separation of the muriate of ammonia, gave a deliquescent chloride, which, when decomposed by an alkali, furnished a combustible gas possessing the strong odour of æthylamine. The condensation of the dried gas in a freezing mixture furnished a clear fluid, which began to boil at the ordinary temperature, and possessed all the physical properties of æthylamine. The platinum-salt, when ignited, furnished 38·62 per cent. of platinum; calculated, 39·4 per cent. The slight difference in the result is to be ascribed to the small quantity of the salt employed. The determination, however, was made principally to ascertain whether the base was æthylamine or bi- or triæthylamine. The author obtained better results with sulphovinate of lime than with the corresponding potash-salt.

From their ready solubility, the salts must be well dried, as a small quantity of water suffices to convert them into a doughy mass, or even to render them fluid. For the same reason, it is advisable to mix the urea with the lime first, and then to add the sulphovinate of lime.—Liebig's *Annalen*, March 1857, p. 288.

On a new Derivative of Anisic Acid. *By* F. Pisani.

Anisic acid being a monobasic acid, possessing a chloride and an amide, should also have its anhydrous acid, like benzoic acid. The

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author has prepared this anhydrous acid by treating anisate of soda with oxychloride of phosphorus, according to Gerhardt's process:—

$$6\left.\begin{matrix}C^8H^7O^2\\Na\end{matrix}\right\}O + PCl^2O = \left.\begin{matrix}PO\\Na^3\end{matrix}\right\}O^3 + 3\left.\begin{matrix}Na\\Cl\end{matrix}\right\} + 3\left.\begin{matrix}C^8H^7O^2\\C^8H^7O^2\end{matrix}\right\}O.$$

The anisate of soda must be previously dried, then reduced to powder, and heated in a balloon with the quantity of oxychloride of phosphorus required by theory. When the reaction is completed, the mass is treated with cold water and filtered. The anhydrous acid which remains on the filter is washed, pressed between bibulous paper, and then crystallized from æther.

It crystallizes in small silky needles, grouped round a common centre. It is insoluble in water, and fuses in that liquid at a boiling temperature. Alcohol and æther dissolve it readily, especially when heated; it is more soluble in a mixture of the two. It is insoluble in potash and ammonia, and these alkalies only convert it into the ordinary acid by the aid of heat. Long boiling with water effects the same transformation. It fuses at about 210° F., and distils at a higher temperature. Its analysis gave—

	Found.	Calculated, $\left.\begin{matrix}C^8H^7O^2\\C^8H^7O^2\end{matrix}\right\}O$.
C	66·95	67·13
H	5·17	4·89

On the Action of Heat upon Anisate of Ammonia.—The ammoniacal salts of benzoic acid, cuminic acid, and some other organic monobasic acids, when heated furnish a nitrile, with evolution of water. The author thought that anisate of ammonia would have given the same reaction, but this salt, when heated, splits into ammonia and ordinary anisic acid, the latter possessing its usual properties and crystalline form, but having its melting-point raised a few degrees. The analysis of the acid gave—

	Found.		Calculated, $\left.\begin{matrix}C^8H^7O^2\\H\end{matrix}\right\}O$.
C	62·75	62·99	63·15
H	5·28	5·40	5·26

Comptes Rendus, April 20, 1857, p. 837.

Moulds of Stearic Acid and Shell-lac for Galvanoplastic Copies. *By* M. Piil.

The best material for moulds is prepared from equal parts of stearic acid and shell-lac. The stearic acid is melted first, and the shell-lac is then added in small fragments; the mass is heated until it may be ignited. It is allowed to burn until the shell-lac which has been separated from the stearic acid by the great heat, may be again combined with it. It is burnt until a drop let fall upon a cold metal plate receives the black lead readily after its solidification. The mass is poured into a paper box, and its surface rubbed with black lead.—*Polyt. Notizblatt*, No. 13, p. 193.

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THE CHEMICAL GAZETTE.

No. CCCLII.—June 15, 1857.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Benzamic Acid. By H. SCHIFF.

BÉCHAMP'S method of reduction by means of iron and acetic acid has hitherto only been employed in the reduction of nitro-bases or indifferent nitro-compounds. This method, however, is capable of a far more general application, and may also be extended to nitro-acids and their derivatives. Nitrobenzoic æther is quickly converted by it into benzamic æther.

Nitrobenzoic æther was for this purpose triturated with twice its weight of iron filings, and mixed with acetic acid to the consistence of a paste. The mixture was slightly heated, when the reaction immediately occurred. The excess of acetic acid passes over into the receiver, and the retort finally contains a blackish-brown mass, consisting of benzamic æther and acetate of iron. The former is extracted with hot absolute alcohol, on the evaporation of which it remains as a thickly fluid yellow substance. This æther was boiled with alcoholic solution of potash, and the fluid neutralized with muriatic acid after the completion of the decomposition. On cooling, crystalline warts of benzamic acid were obtained; the mother-liquor, when evaporated, also deposited a further small quantity, which was freed from chloride of potassium by washing with cold water. The recrystallized acid was of a pale red colour, dissolved readily in alcohol and hot water, and its concentrated solutions gave with strong nitric acid, sulphuric acid, and muriatic acid shining needles of the corresponding compounds.

By boiling with carbonate of baryta, the baryta-salt was prepared; it gave on analysis 33·47 per cent. of baryta. The formula $C^{14} H^6 BaNO^4$ would require 33·52 per cent.

In the preparation of larger quantities of benzamic acid, in which the extraction of a mixture of benzamic acid and acetate of iron with absolute alcohol would be too expensive, and in the employment of aqueous alcohol the solution of the iron salt could not be avoided, the following process is advisable. The mixture of iron filings and nitrobenzoic acid is mixed with acetic acid in a spacious dish; after the reaction has taken place, the excess of acetic acid is evaporated on the water-bath, the dry mass is pulverized, and the benzamic acid extracted with solution of potash. The solution is evaporated to a small volume, and mixed with acid; the benzamic

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acid is then precipitated in a nearly pure state, and purified by one recrystallization from alcohol. Besides the various potash-salts, the mother-liquor still contains some benzamic acid; it is therefore evaporated to dryness, and extracted with a little absolute alcohol.

Gerhardt and others have already indicated how very unsuitable the denomination "benzamic acid" is for this compound. Under the term aminic acid we understand an acid amide, deriving from the type $\left.\begin{matrix}NH^4\\H\end{matrix}\right\}O^2$, in which the radical of the corresponding acid replaces hydrogen in the ammonium. But neither benzamic acid nor the aminic acid of any other monobasic acids can be referred to this type. The name of "amidobenzoic acid" has therefore been proposed for the present compound, but the author does not think that any new name is necessary. Since Gerland has proved that benzamic acid is identical with the carbanilidic acid prepared by Chancel by boiling carbanilamide with solution of potash, it appears to the author that benzamic acid would be best characterized as carbanilidic acid or phenylocarbaminic acid, in which case it would have the rational formula $\left.\begin{matrix}NH.C^{12}H^5.C^2O^2\\H\end{matrix}\right\}O^2$, deriving from the type $\left.\begin{matrix}NH^4\\H\end{matrix}\right\}O^2$. This also applies to amidocuminic and amidocinnamic acids, which are to be regarded as true aminic acids, the former as cumenylocarbaminic acid, $\left.\begin{matrix}NH.C^{18}H^{11}.C^2O^2\\H\end{matrix}\right\}O^2$, homologous with phenylocarbaminic acid, and the latter as styrylocarbaminic acid, $\left.\begin{matrix}NH.C^{16}H^7.C^2O^2\\H\end{matrix}\right\}O^2$. We should not be by any means surprised at seeing derivatives of benzoic acid converted into compounds of phenylocarbonic acid under the influence of strong agents, for we know how easily formic acid yields carbonyle (carbonic oxide gas), and according to Gerhardt benzoic acid is essentially nothing but phenyloformic acid, as we endeavour to express by the formula $\left.\begin{matrix}C^2(C^{12}H^5)O^2\\H\end{matrix}\right\}O^2$. Moreover, phenylurea, which according to Natanson is phenylocarbamide, is produced by the reduction of nitrobenzamide.

Without taking into consideration its decomposability into aniline and carbonic acid at a high temperature, the mode of production of benzamic acid is peculiarly in favour of the above formula.

First, as regards its formation from benzoic acid. If we were to become acquainted with a formic acid, the hydrogen in whose radical might be replaced by hyponitric acid, this would be decomposed by reducing agents in accordance with the following equation:—

$$\left.\begin{matrix}C^2(NO^4)O^2\\H\end{matrix}\right\}O^2+6H=\left.\begin{matrix}NH^2C^2O^2\\H\end{matrix}\right\}O^2+4HO,$$

that is to say, an acid would be produced which would be carbaminic acid. But a nitroformic acid is still unknown, as well as the nitro-acid of any acid of the series of fatty acids of the formula

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$C^{2n}H^{2n}O^4$ (unless we except propionic and valerianic acids); but we certainly know a nitroformic acid in which hydrogen is replaced in the radical by phenyle, $C^{12}H^5$, and this is nitrobenzoic acid. Now if carbaminic acid makes its appearance as a product of the reduction of nitroformic acid, a phenylocarbaminic acid (carbanilidic acid) must also be obtained by the reduction of phenylonitroformic acid. But the acid which makes its appearance in this reduction is benzamic acid.

A second mode of preparation is that of Chancel, from carbanilamide. The amides of the bibasic acids are decomposed under the influence of 1 equiv. of hydrate of potash, into ammonia and the potash-salt of the corresponding aminic acid; in this case, therefore, carbamide is decomposed into ammonia and carbaminate of potash, in accordance with the equation—

$$N^2\left\{\begin{matrix}C^2O^2\\H^4\end{matrix}\right. + KaHO^2 = NH^3 + \left.\begin{matrix}NH.C^2O^2\\Ka\end{matrix}\right\}O^2;$$

but according to this it must furnish phenylocarbamide-ammonia and phenylocarbaminate of potash. But the potash-salt which Chancel obtained by this process was that of carbanilidic acid, which is identical with benzamic acid.

Carbaminic acid is produced from carbonic acid and ammonia, $NH^3 + C^2O^4 = \left.\begin{matrix}NH^2.C^2O^2\\H\end{matrix}\right\}O^2$. In the same way, phenylocarbaminic acid would be produced from aniline and carbonic acid:—

$$N\left\{\begin{matrix}C^{12}H^5\\H^2\end{matrix}\right. + C^2O^4 = \left.\begin{matrix}NH.C^{12}H^5.C^2O^2\\H\end{matrix}\right\}O^2.$$

When the author brought together vapours of aniline and carbonic acid with this object, thick white clouds were immediately produced, which however he did not succeed in condensing. By longer action in the cold, a small quantity of a white crystalline coat was formed, and this, when dissolved in water, gave it an acid reaction.

Of the same empirical composition with benzamic acid, and very similar to it in its compounds, is the anthranilic acid prepared by Fritzsche from indigo, for which the name of phenylocarbaminic acid has hitherto been adopted as the rational denomination. But if we consider that this acid furnishes salicylic acid by deamidation, it may perhaps rather be regarded as a compound nearly approaching the salicyle group. That in the form in which it has hitherto been investigated anthranilic acid is not identical with salicylaminic acid, has already been proved by Limpricht. However, these two acids nearly agree in their melting-point and some other properties.

In benzamic acid, as in anthranilic acid, nitrous acid separates the elements of the amide, and hydrogen takes the place of the latter. The acid thus produced, called oxybenzoic acid by Gerland, has the same composition as salicylic acid, but differs therefrom in its properties.

As it is produced from an acid which contains the two radicals carbonyle and phenyle, the derivative will probably also contain

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these two radicals; and this can hardly be otherwise, as these radicals are not altered by nitrous acid, but, as the final result of the action, the elements NH are separated and 2O added. Here therefore we have $N.C^2O^2.C^{12}H^5.H^2O^2 - NH + 2O = C^2O^2.C^{12}H^5.HO^4$ or $\left.\begin{matrix} C^2O^2 \\ C^{12}H^5.H \end{matrix}\right\} O^4$; but this is nothing more than an acid phenylic æther of carbonic acid, phenylocarbonic acid. This constitution of oxybenzoic acid is supported especially by its decomposability into carbonic acid and phenylic alcohol under the action of hydrate of potash, a decomposition such as also occurs in other compound æthers. This constitution has already been ascribed to salicylic acid by Hofmann and Kolbe. But since Piria has recently proved the bibasic nature of salicylic acid, and phenylocarbonic acid cannot be bibasic, this consitution is no longer admissible for salicylic acid.

In conclusion, it is to be observed that we are also acquainted with a third acid of the empirical formula $C^{14}H^6O^6$, namely, the *ampelic acid* prepared by Laurent. This, however, has not yet been sufficiently investigated to enable us to say anything definite as to its constitution. It occurs in coal-tar oil and the oil of bituminous shale, with other phenyle compounds, and probably stands in close connexion therewith. Wagner asserts that ampelic acid is identical with phenylocarbonic acid.—From the Author's *Inaugural Dissertation*, Göttingen, 1856; *Chemisches Centralblatt*, March 25, 1857, p. 185.

Researches on the Amidogen Acids of the Monobasic Acids. *By* A. Cahours.

The amidogen acids derived from benzoic, toluic, anisic acids, &c., by the reduction of nitrobenzoic, nitrotoluic, nitranisic acids, &c., either by means of hydrosulphate of ammonia or by protacetate of iron, namely benzamic, toluamic, and anisamic acids, &c., behave like true alkaloids, and should be placed in the neighbourhood of glycocoll, alanine, and leucine.

M. Gerland's recent investigation of benzamic acid having shown that it possesses the power of forming crystallizable compounds with nitric and sulphuric acids, the author thought whether it would not be capable of producing similar compounds with the different acids in the manner of glycocoll, and whether the other amidogen acids would not behave in the same way.

He ascertained that benzamic acid forms definite compounds with phosphoric, oxalic, hydrobromic, muriatic, and other acids, and obtained similar compounds of these acids with toluamic, cuminamic, and anisamic acids, which crystallize with the greatest facility.

The muriates formed by these amidogen acids present a composition analogous to that of the muriates of the alkaloids; it is expressed by the formulæ—

$C^{14}H^7NO^4$, ClH, muriate of benzamic acid;
$C^{16}H^9NO^4$, ClH, muriate of toluamic acid;
$C^{20}H^{13}NO^4$, ClH, muriate of cuminamic acid;
$C^{16}H^9NO^6$, ClH, muriate of anisamic acid.

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These different muriates combine with bichloride of platinum, forming distinctly crystallized compounds, represented by the formulæ—

$C^{14} H^{7} NO^{4}, ClH, PtCl^{2}$, chloroplatinate of benzamic acid;
$C^{16} H^{9} NO^{4}, ClH, PtCl^{2}$, chloroplatinate of toluamic acid;
$C^{20} H^{13} NO^{4}, ClH, PtCl^{2}$, chloroplatinate of cuminamic acid;
$C^{16} H^{9} NO^{6}, ClH, PtCl^{2}$, chloroplatinate of anisamic acid.

The first two crystallize in fine golden-yellow needles; the third forms orange needles, and the fourth prisms of a brownish-red colour, which are sometimes of considerable size.

These compounds are most easily obtained by treating the amidogen acid with a slight excess of concentrated muriatic acid, adding sufficient to redissolve the muriate entirely at the boiling temperature, and then adding an excess of bichloride of platinum. The double salt separates entirely on evaporation.

A similar experiment made with muriate of glycocoll gave similar results. A chloroplatinate was obtained in brilliant prisms, of a beautiful orange colour, containing 35 per cent. of platinum; its composition, expressed by the formula $C^{4} H^{5}, NO^{4}, ClH, PtCl^{2}$, agrees exactly with that of the preceding. Besides these characters of relationship, the sulphates of these compounds possess a characteristic saccharine taste.

Like glycocoll, which presents numerous isomers, benzamic acid exhibits two perfectly distinct cases of isomerism, anthranilic acid and salicylamide. Benzamic acid presenting the same relations towards salicylamide, as those between glycocoll and glycolamide, and between alanine and lactamide, it may be asked in what consist the differences observable between bodies which possess the same centesimal composition and the same chemical equivalent.

Salicylic acid, in becoming converted into salicylamide, loses O^{2}, which it exchanges for NH; whilst benzoic acid, in its conversion into benzamic acid, gains NH, without losing oxygen. Hence the relative position of the atoms must be very different in these two compounds, which sufficiently accounts for their different properties.

Glycolamide being produced in the same way of salicylamide, by the reduction of glycolic acid by ammonia, may we not hope to obtain glycocoll by a process similar to that which furnishes benzamic acid, that is, by reducing mononitrated acetic acid by sulphuretted hydrogen. The two reactions should be exactly parallel:—

$$\underbrace{C^{14} H^{5} (NO^{4}) O^{4}}_{\text{Mononitrated benzoic acid.}} + 6SH = 6S + 4HO + \underbrace{C^{14} H^{7} NO^{4}}_{\text{Benzamic acid.}}.$$

$$\underbrace{C^{4} H^{3} (NO^{4}) O^{4}}_{\text{Mononitrated acetic acid.}} + 6SH = 6S + 4HO + \underbrace{C^{4} H^{5} NO^{4}}_{\text{Glycocoll.}}.$$

Chloride of benzoyle, reacting upon the compound of oxide of zinc and glycocoll, gives origin, according to M. Dessaignes, to the

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acid which is met with in the urine of herbivorous animals, hippuric acid. The chlorides of cumyle and anisyle furnish analogous products by their reaction on the compound of oxide of silver and glycocoll. Crystallized acids are obtained, capable of forming crystallizable salts, and splitting in the manner of hippuric acid under the influence of acids and heat, into glycocoll and cuminic or anisic acid. Their formulæ are—

$C^{24} H^{15} NO^6$, cuminuric acid;
$C^{20} H^{11} NO^8$, anisuric acid.

The chlorides of the same radicals acting on a benzamate, a cuminamate, or an anisamate, furnish analogous results. When chloride of benzoyle reacts upon benzamate of silver, the mixture becomes strongly heated by the mutual decomposition which takes place; chloride of silver is obtained, with a new acid which may be isolated by treating the residue with concentrated alcohol, which converts the excess of chloride of benzoyle into benzoic æther. The filtered liquid is evaporated, and then treated with caustic ammonia, which dissolves the acid without touching the benzoic æther. The solution, treated with an excess of muriatic acid, deposits the acid, and this is purified by washing and crystallization from alcohol.

From these facts it appears that between glycocoll, alanine, leucine, and the amidogen acids formed by the monobasic acids, there exist very close relations, whatever may be the rational constitution of these compounds, which it would be impossible to prejudge in the present state of matters.

On the one hand and on the other we have bodies, which, like hydrate of phenyle, unite indifferently with acids and bases, and which can even combine with salts. It is probable that these bodies may be produced by very different processes. It would be curious to try whether the new isomer of cyanic acid recently discovered by Cloëz by the mutual action of chloride of cyanogen and sodium-alcohol, may not be converted into alanine by simple fixation of water, and consequently reproduce with its homologues, glycocoll, leucine, &c. The modes of production of cyanætholine and alanine present the most manifest analogies. Thus we have—

$$\underbrace{C^4 H^4 O^2}_{\text{Aldehyde.}} + C^2 NH + 2HO = \underbrace{C^6 H^7 NO^4}_{\text{Alanine.}};$$

$$\underbrace{C^4 H^5 NaO^2}_{\text{Sodium-alcohol.}} + C^2 NCl = \underbrace{C^6 H^5 NO^2}_{\text{Cyanætholine.}} + Na\,Cl.$$

If we could only succeed in fixing the molecule of hydrocyanic acid upon the molecule of aldehyde without the intervention of water, there is every reason to believe that we should give origin to cyanætholine, the relation between these two substances being exactly comparable to that observed between an amide and its nitrile, or between an alcohol and the corresponding carburet of hydrogen.—*Comptes Rendus*, March 16, 1857, p. 567.

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On the Production of White Sapphires in isolated limpid Crystals, by means of the Blast-furnace, in ordinary Crucibles. By A. GAUDIN.

More than twenty years ago, I obtained artificial rubies by fusing with the oxyhydrogen blowpipe ammoniacal alum with the addition of $\frac{5}{1000}$ths of yellow bichromate of potash. These rubies were identical with native rubies in regard to their chemical composition, their hardness, and colour; but they were deficient in limpidity, in consequence of a partial crystallization which I have as yet been unable to avoid with large globules.

At this period I also obtained a geode of corundum in crystals discernible with the naked eye, and giving the sextuple cleavage peculiar to this mineral; it was produced by fusing a fragment of potash-alum in a crucible of lamp-black with a platinum blowpipe. The blowpipe which hung over the crucible was fused during the operation, so much that several globules of platinum were implanted in the crystals of the geode; before cooling, the globule was limpid, but in crystallizing it became hollow and slightly milky.

500 grms. of the same alum which I sent to Brongniart to be calcined in the porcelain furnace at Sèvres, were converted, to the great astonishment of that celebrated mineralogist, into a heavy mass with brilliant particles, which was a true artificial compact corundum.

When, ten years later, Ebelmen made use of boracic acid, he was not unaware of the part which was played by potash in the formation of the corundum of Brongniart his predecessor; but the series of characteristic crystals which he was able to make by this means, constituted a work out of the direct line, which I admired as much as any one, so much indeed that I never made any reclamation when I found that in the historical account of his researches mine were entirely omitted; and if I speak of it now, it is to show that my new results also possess a character which distinguishes them from his.

In fact, I wished to obtain, not concretions, like Ebelmen, by *completely* evaporating the solvent, but rather isolated crystals, by evaporating the solvent *partially* or by originating a slow refrigeration, suited to increase crystals suspended in a pasty liquid. It is to the realization of these two conditions that the first success which I have to submit to the Academy is to be attributed.

To produce limpid crystals of alumina, I introduce into a common crucible, luted with lamp-black, equal parts of alum and bisulphate of potash, previously calcined and reduced to powder, and submit the crucible to the violent heat of a blast-furnace for a quarter of an hour. On breaking the crucible, we find in the hollow of the luting a concretion bristling with brilliant points; this consists of sulphuret of potassium imbedding the crystals of alumina. With nitromuriatic acid diluted with water, a precipitate resembling fine sand is obtained; this is washed with several waters.

This process does not allow of the production of coloured stones, on account of the reducing power of the carbon, which converts all the colouring oxides into metallic globules.

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The crystals are larger in proportion to the size of the masses operated on, and consequently to the duration of the calcination; those which I obtained with my little blast-furnace attain a size of 1 millim. and a thickness of $\frac{1}{3}$ millim.

Their hardness is excessive, for M. Gindreaux, our clever lapidary, has assured me that he found them harder than the native rubies, which he employed for the holes in watch-work. It took him twenty minutes to pierce one of them with a drill of $\frac{1}{10}$th millim. in diameter, making 100 turns in a second, so that it required 120,000 turns of the drill to pierce the sapphire.

The limpidity of these crystals is extreme; with a microscope of Oberhäuser and Hartnack and a power of 300 diameters, the bases of the rhombohedra exhibit equilateral triangles formed by lines of exquisite purity.

According to my researches, it is the sulphuret of potassium that becomes a solvent of alumina, for the same crystals are obtained by placing calcined alumina in the luted crucible, with some sulphuret of potassium. Consequently the sulphurets, the fluorides, the cyanides, and, in a word, the binary compounds, presenting considerable resistance to decomposition and volatilization, may furnish us with the means of obtaining a great number of insoluble crystals. We may perhaps even succeed, with fires fed with oxygen, in finding a solvent for carbon, capable of furnishing the perfect diamond. And this is so true, that in trying to produce silica by these means, I have already obtained a smoky glass, free from aluminium and boron, which scratches the ruby. I obtained this singular body by placing in my luted crucible silicate of potash and sulphuret of potassium.—*Comptes Rendus*, April 6, 1857, p. 716.

Preliminary Note on the Tannin of Galls. *By* F. Rochleder.

The author long since stated, that the treatment of certain organic substances with boiling alkaline solutions in an atmosphere of hydrogen furnished a good means of breaking them up. This process has been applied by Kawalier, in the author's laboratory, to various substances. Several bodies which furnish crystallized sugar when treated with dilute acids with the aid of heat, also furnished this sugar when treated in this way with alkalies; thus, for example, a yellow crystallized substance from the twigs of *Thuja occidentalis* may be decomposed by alkalies, as also by acids, in hydrogen gas, into well-crystallized grape-sugar, and a yellow crystalline body, similar to quercetine, which acquires a beautiful bluish-green colour with ammonia. The author has also induced Kawalier to submit the tannin of galls to this treatment. In this way is obtained gallic acid, which may easily be procured pure by this process, and an amorphous yellowish body, of a somewhat bitter and acid taste, similar to gum-arabic, which on analysis gave numbers corresponding with the formula $C^{12}H^{11}O^{11}$. From about 150 grms. of tannin, not 1 milligrm. of sugar was formed. The fluid freed from gallic acid reduced no trace of protoxide of copper from Fehling's fluid.

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Further experiments, which Kawalier has commenced with larger quantities of tannin, will serve to determine the atomic weight of the amorphous body.—*Sitzungsber. der Akad. der Wiss. zu Wien*, xxii. p. 558.

Examination of a Nickel Meteorite, from Oktibbeha County, Mississippi. By WILLIAM J. TAYLOR.

This highly interesting and unique meteorite was found in an Indian mound, in which excavations were being made in a search for Indian antiquities, in Oktibbeha County, Mississippi. It then weighed $5\frac{1}{4}$ oz.; in shape it resembled a hen's egg. When found, there was a fissure which divided it almost equally into two parts. The person who discovered it seeing this, placed it upon an anvil, and with one blow of a sledge-hammer divided the meteorite. One half was forged, with the intention of manufacturing it into a cutting instrument of some description; the other remained in its original state, excepting that its exterior was filed smooth and bright.

To Dr. William Spillman, of Columbus, Mississippi, I am indebted for the material for this investigation; he obtained the meteorite from the man who first found it. The unforged half he brought with him on a recent visit to this city, and a portion of which he has presented to the Academy, on the condition that it should be carefully cut, so that the surface which formed one side of the existing fissure above mentioned should be preserved and sent to him. It was proposed to have it cut by a lapidary, but he attempted it without success, using diamond-dust on the wheel. On making the first incision, about one-eighth to one-sixteenth of an inch in depth, he found it impossible to proceed, and refused to make further attempts to cut the meteorite. Mr. John Phillips, a fellow member of the Academy, and an amateur machinist, on hearing of our difficulties, kindly offered to saw the specimen, and succeeded admirably, though it was with very great difficulty. He spoke of its peculiar toughness (the hardness not being excessive); it resisted the saw very much, which rendered the cutting exceedingly tedious, heating the saw to such a degree as to oblige a discontinuance of the operation every four or five minutes; but it was remarkable that it did not dull the blade in the least.

The toughness of the iron was clearly shown, when, for the purpose of analysis, it was attempted to cut off portions of it with a chisel; the excessive toughness of the iron rendered this very difficult without the aid of the saw. The resistance of this meteorite to the action of acids was most remarkable. Strong nitric acid did not act upon it in the cold. Moderately dilute sulphuric acid did not act upon it. Strong and boiling hydrochloric acid acted upon it very gradually.

The above-named acids failing to show the slightest trace of the Widmannstättian figures, a mixture of nitric acid and hydrochloric was used, boiling; but even after this operation no trace of them could be distinguished. The action of the aqua regia was gradual

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and peculiar, producing on the polished surface of the meteorite very small holes, varying in size from a pin's point to those as large as a pin's head. From the appearance of the surface of the meteorite, which formed a side of the fissure before described, I had hoped to obtain by etching beautiful Widmannstättian figures, as there is on this portion indistinct traces of that which would at first glance be called a crystalline structure.

The colour of the metal is a silvery gray with a pinkish tinge. Its hardness is not excessive, yielding readily to the file. The tensibility, as before mentioned, was very great. The passivity was proved by testing it with a neutral solution of the sulphate of copper.

The specific gravity at 25° Cels. was found by Dr. F. A. Genth to be 6·854, which is too low; but owing to the numerous fissures through the meteorite filled with limonite, it was impossible to obtain the exact specific gravity of the metal. I used particular care to obtain a portion free from the flaws, but without effect. I take this opportunity to express my thanks to Dr. Genth for allowing me the use of his laboratory in making the examination. The following is the result of my analysis:—

1·9421 grm. dissolved in aqua regia gave:—

1·4731 grm.	NiO	=	nickel	59·69	per cent.
1·0452 ...	Fe^2O^3	...	iron	37·69	...
0·0221 ...	CuO	...	copper	0·90	...
0·0072 ...	Al^2O^3	...	aluminium	0·20	...
0·0105 ...	Co^6O^7	...	cobalt	0·40	...
0·0048 ...	SiO^3	...	silicium	0·12	...
0·0069 ...	$2MgO, PO^5$	...	phosphorus	0·10	...
0·0059 ...	CaO, CO^2	...	calcium	0·09	...
				99·19	

The slight loss of $\frac{8}{10}$ths of 1 per cent. I think is owing to some small portions of limonite existing in the minute fissures already mentioned.

The 0·10 per cent. of phosphorus correspond to 0·64 per cent. of schribersite ($P.Ni^2Fe^4$).

It was first attempted to dissolve in hydrochloric acid, but the action of the acid, even when boiling, was so very gradual that nitric acid was added.

I endeavoured to separate the nickel and cobalt by Liebig's new method, viz. by precipitating the nickel as a sesquioxide, by passing chlorine through an alkaline solution of the two metals in hydrocyanic acid and potash, but it was found not to answer; the separation was made by his former method by oxide of mercury.

The composition of this remarkable meteorite is in itself sufficiently interesting for mineralogists, without any attempts to account for its origin, either terrestrial or celestial. We must remain in doubt as to the exact locality where it was originally found, as it may have been carried by the Indians from a distance to be entombed in this mound, and it may have been considered by them to have a

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special value, and possibly to possess peculiar virtues, from its being discovered in such a place.—From the *Proceedings of the Academy of Natural Sciences of Philadelphia*, April 1857.

On the Formation of Phosphovinic Acid in the Preparation of Iodide of Æthyle. *By* D. K. Tuttle.

In the preparation of iodide of æthyle from alcohol, phosphorus, and iodine, in the proportions directed by Frankland, there remains in the retort, after the distillation of iodide of æthyle, a considerable quantity of a syrupous fluid together with the excess of phosphorus. It exhibits a strongly acid reaction, which has been attributed to the presence of phosphoric acid. Thinking it improbable that free phosphoric acid would exist under these circumstances, the author diluted the fluid, and neutralized it with carbonate of baryta. Instead of insoluble phosphate of baryta, he obtained a considerable amount of a soluble salt, which did not appear to be easily crystallizable, but was easily obtained in a pure state by precipitation with alcohol, in which it is insoluble. A small quantity of alcohol sufficed to render the aqueous solution turbid, and the salt then separated as a light crystalline powder. Heated over the spirit-lamp, it burnt, leaving an insoluble residue, apparently of pyrophosphate of baryta.

A quantity of the salt, dried at 212° F., was heated to 284° F. without losing further in weight; it is consequently anhydrous.

0·3505 grm., dissolved in water and precipitated with sulphuric acid, gave 0·3092 of sulphate of baryta, representing 57·88 per cent. of baryta. Phosphovinate of baryta, $\frac{C^4 H^5 O}{2BaO} PO^5$, requires 58·3 per cent., but the identity of the two admits of no doubt. The fluid residue of the distillation of iodide of æthyle is therefore free phosphovinic acid.—Liebig's *Annalen*, March 1857, p. 290.

On the Compounds of Tantalum with Nitrogen. *By* H. Rose.

If ammoniacal gas be passed over tantalic acid at a strong red heat, it is but slightly decomposed. The grayish powder obtained contains only a little nitruret of tantalum, although it evolves ammonia when fused with hydrate of potash; it consists for the most part of undecomposed tantalic acid.

If gaseous cyanogen be passed over tantalic acid at a red heat, a brown powder is obtained; this contains nitruret of tantalum and cyanide of tantalum, but also a great deal of undecomposed tantalic acid, and therefore does not conduct electricity.

Nitruret of tantalum is obtained in the greatest purity when perchloride of tantalum is submitted to the action of gaseous ammonia. The reduction of the perchloride and the expulsion of the chloride of ammonium only take place completely at a strong red heat. Nitruret of tantalum is a black powder, which acquires a metallic

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lustre when rubbed in an agate mortar; it exhibits a crystalline structure under the microscope, conducts electricity very well, evolves a great quantity of ammonia when fused with hydrate of potash, is not attacked by nitric acid and nitromuriatic acid, but is strongly acted upon by a mixture of nitric and hydrofluoric acids. Its composition is probably 3Ta+2N.—*Bericht der Akad. der Wiss zu Berlin*, 1857, p. 16.

On the Decompositions of Aqueous Solutions of Bisulphite of Aldehyde-ammonia by Heat. *By* T. Petersen.

Bisulphite of aldehyde-ammonia in solution in water furnishes a series of decompositions, which partly consist in the conversion of the sulphurous acid into sulphur and sulphuric acid, but partly relate to the aldehyde itself. In carrying on the investigation, the solid salt was dissolved in water and exposed for some time to a gentle heat, or the mother-liquor was employed when it had stood for a long time and gradually acquired an unpleasant odour.

The fluid was put into a retort, and distilled with a thermometer immersed in it. When the boiling-point had passed 212° F., an ammoniacal fluid first of all passed over, and a separation of sulphur commenced and gradually increased in the retort. As the boiling-point rose, an extremely disagreeable garlic-like odour constantly became stronger. Between 257° and 302° F. single oily drops passed into the distillate; these floated on the surface, but nevertheless, when put into a narrow cylindrical glass with pure water, they sank to the bottom, so that their specific gravity appeared to be nearly equal to that of water. In the cold they were not altered by acids, but they were slowly decomposed thereby, with deposition of sulphur, when heated. Their garlic- and onion-like odour was extremely insupportable. This body was obtained in the largest quantity when the contents of the retort were brought to dryness by as low a temperature as possible, again treated with water, and more strongly heated.

These properties, and especially the odour, characterized the compound as bisulphuret of æthyle, which was further shown to be the case by analysis:—

C	..	4	39·34
H	..	5	8·2
S	51·8	2	52·46

Bisulphuret of æthyle, or the so-called thialole, was prepared by Zeise by the distillation of polysulphuret of potassium with sulphovinate of potash, and by Löwig with the same sulphuret and acid oxalic æther.

Löwig and Weidmann have also shown that this body is produced from mercaptan when the latter is heated with moderately strong nitric acid, and the oil which sinks to the bottom, the sulphite of sulphuret of æthyle, $C^4 H^5 S^2 O^4$, is decomposed by potash.

Besides bisulphuret of æthyle, the distillate at the above-mentioned boiling-point contains especially acetic acid and sulphurous acid combined with ammonia, as well as polysulphuret of ammonium.

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The oily drops of bisulphuret of æthyle were removed and muriatic acid was added, by which sulphurous acid was evolved in considerable quantity, and sulphur was thrown down, a reaction which allows us to conclude with certainty that polysulphuret of ammonium was present. When the acid solution was heated, the odour of acetic acid was evolved, and perchloride of iron showed the presence of this acid still more decidedly.

As soon as the boiling-point in the retort had risen to 302° F., the odour of bisulphuret of æthyle gradually disappeared. The residuary mass had then become thick and acquired a brown colour, and a partial carbonization had commenced. At the same time crystals of carbonate of ammonia were deposited in the neck of the retort, and indeed carbonic acid was to be detected throughout the whole course of the distillation. Its presence was ascertained by testing for it with baryta-water.

When the odour of bisulphuret of æthyle had disappeared, another one was recognized, which appeared to arise from a volatile amine base. Some muriatic acid was therefore put into the receiver, and the distillation was continued as long as volatile products made their appearance, and until the contents of the retort became quite dry. The solution in muriatic acid was evaporated; the salt, which consisted for the most part of muriate of ammonia, was extracted with alcohol and æther, and the solution obtained was precipitated with bichloride of platinum. The double salt thus procured exhibited the composition of the platinochloride of bimethylamine. Its analysis gave—

C	..	..	4	9·57
H	..	..	8	3·19
N	..	..	1	5·58
Cl	..	..	3	42·35
Pt	39·628	39·344	1	39·31

With the appearance of the volatile amine base the decomposition of bisulphite of aldehyde-ammonia is completed. The solid residue in the retort, which had partly extended upwards on its walls in the form of a white salt, contained, besides a spongy coal and sulphur, sulphate, sulphite, acetate, and carbonate of ammonia.—From the author's *Inaugural Dissertation*, Göttingen, 1857.

On a Modification of the Bisulphite of Aldehyde-ammonia.
By T. Petersen.

The preparation of bisulphite of aldehyde-ammonia is effected, according to Redtenbacher, in the following way. The fluid obtained by distillation from 2 parts of alcohol of spec. grav. 0·863, 3 parts of brown oxide of manganese, 3 parts of sulphuric acid, and 2 parts of water, is rectified in the water-bath, then mixed with chloride of calcium, the aldehyde distilled off at 68° to 86° F., mixed with æther, and ammonia passed into it. The crystals of aldehyde-ammonia separated are then again dissolved in alcohol and the solution saturated with sulphurous acid, when the bisulphite of

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aldehyde-ammonia gradually separates. This salt forms granular or somewhat laminar masses; it is slowly altered at ordinary temperatures, and more rapidly at 212° F. It cannot be recrystallized, and as Redtenbacher remarks, only a few more crystals are deposited from the mother-liquor after some time, although from the quantity of materials employed a large quantity of salt must still remain in the fluid.

If ammoniacal gas be passed into the solution of aldehyde in alcohol and æther, crystals of aldehyde-ammonia are separated, and these, if left standing in the fluid, soon deliquesce again. The solution afterwards deposits no more of the salt, but a yellow stratum is formed at the bottom of the vessel; this is deliquesced aldehyde-ammonia. The whole of this fluid was then gently heated in a flask, in order to drive off as much as possible of the alcohol and æther, when acetic acid and acetic æther were evolved in small quantity; the latter was also detected by Liebig amongst the bodies produced during the formation of aldehyde. The solution, which had become brown, was then saturated with sulphurous acid, when it again acquired a paler colour, but no solid compound was deposited. But when it was very carefully evaporated, crystalline crusts of a somewhat yellow salt separated; this was obtained white by washing with alcohol. The same compound was obtained when the solution was set aside for some time. This body possesses the composition of bisulphite of aldehyde-ammonia. On one occasion acicular crystals separated during the passage of the sulphurous acid, and these readily volatilized with the appearances described by Liebig for metaldehyde; it was impossible, however, to make any closer examination of this body, from its being in too small quantity.

The compound obtained in the above way forms crystalline crusts, which under the microscope appear to be an aggregation of small needles. It may be recrystallized, and is then obtained in aggregations of small columnar crystals. Analysis:—

C	18·561	19·1	4	19·2
H	5·845	..	7	5·6
N	11·214	11·21	1	11·2
O	..	..	6	38·4
S	25·94	25·7	2	25·6

This salt remains unchanged at ordinary temperatures and when heated to 212° F.; it is only decomposed when heated to 302° F. It dissolves in water, especially in the cold, with much more difficulty than Redtenbacher's salt. These properties, combined with the difference in its external appearance and with the recrystallizability of the salt, form a series of characters by which the two compounds may be distinguished from each other.

The solutions of this bisulphite of aldehyde-ammonia evolve aldehyde and sulphurous acid when treated with an acid with the assistance of heat.—From the author's *Inaugural Dissertation*, Göttingen, 1857.

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ANALYTICAL CHEMISTRY.

Volumetric Determination of the Amount of Zinc in Ores and Metallurgical Products. *By* MAX SCHAFFNER.

THE method here described is intended to furnish the zinc-smelter with a means of testing his ores and metallurgical products for their amount of zinc with sufficient, although not with perfect accuracy.

The principle of the method is as follows:—Oxide of zinc dissolves very readily in a mixture of caustic ammonia and carbonate of ammonia, a property which Schmidt has already made use of in the analysis of calamine. From this ammoniacal solution the zinc is completely precipitated by sulphuret of sodium. Now if exactly so much sulphuret of sodium is added as is necessary for the precipitation of the zinc, the amount of zinc may be calculated from that of the sulphuret of sodium employed. It is impossible, however, to observe the moment exactly when the necessary quantity of sulphuret of sodium has been added, for which reason it is necessary to call in the aid of another reaction, which shows the completion of the operation with certainty. This object is very simply and perfectly attained when a few drops of perchloride of iron are added to the ammoniacal solution, by which a voluminous red precipitate of hydrated oxide of iron is produced. If sulphuret of sodium be then added, this red precipitate remains unchanged as long as the solution still contains zinc; but as soon as all the zinc is thrown down as hydrated sulphuret of zinc, the red suspended precipitate of hydrated oxide of iron becomes black, sulphuret of iron being formed; and this is the sign that the operation is completed, that is to say, that sufficient sulphuret of sodium has been added.

The valuation of the sulphuret of sodium is effected in the following way:—About 0·2 grm. of chemically pure zinc is weighed and dissolved in muriatic acid in a flask; the ammoniacal fluid is then added, and afterwards the same number of drops of perchloride of iron which will be used in the analysis. Sulphuret of sodium is then poured in from the burette until the red precipitate appears black, the number of cubic centimetres employed is noted, the quantity serving for the blackening of the oxide of iron is deducted, and from this is calculated how much zinc is represented by 1 cub. centim. of sulphuret of sodium. Instead of valuing the solution of sulphuret of sodium with pure zinc, which must be weighed off every time, a normal solution of sulphate of zinc with an excess of ammonia may be made use of. For this purpose a quantity of sulphate of zinc is weighed off, dissolved in water, mixed with an excess of ammonia, and brought to a certain volume, say about 1000 cub. centims. It may then easily be calculated how much zinc is contained in 1 cub. centim. of this solution. For the valuation of the sulphuret of sodium a certain number of cubic centimetres of this solution may be employed every time, the process being the same as with pure zinc. The dilution of the sulphuret of

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sodium is about right when 17 to 18 cub. centims. represent about 0·2 grm. zinc.

To determine the quantity of sulphuret of sodium required to convert oxide of iron into sulphuret, the following is the process adopted. Into a glass flask is put about as much water containing ammonia as there is fluid obtained in the analysis; to this is added the same number of drops of perchloride of iron as is employed in the analysis, and after this the solution of sulphuret of sodium until the red colour of the precipitate has become converted into black. When well corked, the solution of sulphuret of sodium remains for some time without alteration; it is, however, better to test it again when it has been standing for some days, especially as the new testing does not occupy more than 8 to 10 minutes.

1 grm. of substance is usually quite sufficient for investigation. With very poor substances, residues of distillation from muffles, &c., it is better to take 2 grms.; with very rich substances 0·5 grm. is sufficient.

The mode of performance of the analysis varies somewhat according to the nature of the substance to be investigated, in which silicate of zinc (both the hydrated and the anhydrous), which is not usually reckoned amongst the smeltable ores, must also be numbered according to the experiments made. The objects of investigation may therefore be—

A. Metallic products, oxides, carbonates, sulphates;

B. Silicates of zinc (anhydrous and hydrated), mixtures of carbonates and silicates;

C. Sulphurets (blende).

With A, 1 grm. of substance is weighed off, and dissolved in a flask, with the aid of a gentle heat, in muriatic acid to which a few drops of nitric acid have been added (for the oxidation of the iron). The free acid is then saturated with caustic ammonia, and the whole is supersaturated with ammonia to which about $\frac{1}{4}$th of carbonate of ammonia is added; it is heated in a shallow, open porcelain dish, by which at the same time almost all the manganese is separated in the form of hydrated oxide. Any precipitate produced is separated by filtration, and washed with water containing ammonia; to the filtrate which now contains all the zinc in solution, 4 drops of perchloride of iron are added from a burette, and then the standard solution of sulphuret of sodium is added from another burette until the above-mentioned reaction makes its appearance, that is, until the red precipitate of hydrated oxide of iron appears black. The number of cubic centimetres of sulphuret of sodium employed is read off, the quantity required for the blackening of the oxide of iron is deducted, and the amount of zinc calculated therefrom. Suppose 1 grm. of substance has been weighed and 23 cub. centims. of sulphuret of sodium employed for the completion of the analysis, of which 1 cub. centim. represents 0·0111 grm. zinc, and also 1·5 cub. centims. of sulphuret of sodium have been used for the blackening of the oxide of iron, the amount of zinc would be $=(23-1{\cdot}5).0{\cdot}0111=0{\cdot}23865$, or 23·865 per cent.

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B. If silicates of zinc are to be investigated, the substance is mixed in a porcelain dish with muriatic acid to which a few drops of nitric acid have been added; the whole is evaporated to dryness, in order to separate the silica completely; the mass is drenched with water with the addition of a few drops of muriatic acid; the ammoniacal fluid is added; it is warmed, filtered, and treated as above.

C. Crude blende, in a finely-powdered state, is treated with nitro-muriatic acid in a flask until the sulphuret of zinc is decomposed and only a little yellow sulphur swims on the surface, when the ammoniacal fluid is added. The rest of the process is the same as above.

When copper occurs with the zinc, as is the case in many blendes, this does not interfere with the determination of the zinc unless it be in too large quantity, as the copper may be determined by the same analysis according to the method of Pelouze. The copper passes into the ammoniacal solution, and colours this blue. The proper number of drops of perchloride of iron is added, the whole is heated until it begins to boil, and the addition of the sulphuret of sodium then commences. The copper is first thrown down as a black precipitate ($5CuS+CuO$); the fluid has then lost its blue colour, and instead of the black precipitate, a white one of sulphuret of zinc suddenly begins to form. The number of cubic centimetres made use for the copper is then read off, and the addition of sulphuret of sodium is continued until all the zinc is precipitated and the suspended hydrated oxide of iron has become black. The numbers are again read off, and the amount of zinc is calculated as above described. If a large quantity of copper were present, which however is rarely the case, the greater part of the copper is first precipitated and separated by filtration, and then the filtrate is treated as described. When the amount of copper is to be calculated, the sulphuret of sodium must of course be valued against copper. This is done by dissolving about 0·2 grm. of pure copper in nitric acid, supersaturating it with ammonia, heating the solution in a flask to the commencement of boiling, and then adding sulphuret of sodium until the blue colour has disappeared and no more black precipitate is formed. The quantity of copper represented by 1 cub. centim. of sulphuret of sodium is then calculated.

The application of heat, which is necessary when the ammoniacal solution contains copper, is not at all injurious to the determination of the zinc; nay, it is even advantageous in the simple determination of zinc to warm the ammoniacal solution, as in this case the reaction takes place much more rapidly and distinctly. Nickel and cobalt are also dissolved in the ammoniacal fluid, but they are extremely rare constituents of zinc ores. If they are actually present, which is the case in some blendes, caustic potash may always be employed as a solvent in place of caustic ammonia, without preventing the correct determination of the zinc.

This method has been rejected by Mohr in his work upon volumetric methods. The author asserts that it is by no means so inaccurate as to deserve this, if only care be taken that the ammoniacal solution of zinc is not too concentrated, because then the sul-

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phuret of iron formed cannot settle to the bottom out of the thick mass of sulphuret of zinc. If, on the contrary, the solution of zinc be diluted and the solution of perchloride of iron very concentrated, the separation is very complete and distinct. Moreover, the fluid in the flask must not be agitated, but, by a skilful turning round, a rotating motion is given to the contents of the flask during the addition of the sulphuret of sodium.—Dingler's *Polytechn. Journal*, cxliii. p. 263.

Investigation of Fluorine. Action of Acids upon Glass.
By J. Nicklès.

The process employed for ascertaining the presence of fluorine in a compound free from silica, consists in evolving the fluorine in the state of hydrofluoric acid, and causing it to react upon a plate of glass; the experiment is formed in a lead or platinum vessel. There is no better process when we have to do with a certain quantity of fluorine.

When the substance to be examined only contains traces of fluorine, and no corrosion can be perceived by the naked eye on the surface of the glass which has been exposed to the vapours evolved during the reaction, the effects produced may be rendered visible by moistening the glass with a little vapour of water, or by breathing on it. The parts attacked then become perceptible, and remain so as long as the slight layer of condensed vapour lasts.

Hitherto this experiment has passed as characteristic of fluorine, and upon it the presence of this metalloid has been admitted in substances which, when treated as above with sulphuric acid, have produced a more or less permanent mark upon a plate of glass. On the faith of this reaction, the presence of fluorine has been admitted in many mineral substances; and if we should be astonished at anything, it is that the same thing has not taken place with fluorine as with any other metalloid which has been met with everywhere, because the reagents intended to detect it contained it. This, in fact, is one of the reasons why this process always succeeds, even with distilled water and the *pure* sulphuric acid of the laboratories; sulphuric acid, purified by any of the known processes, always contains appreciable quantities of hydrofluoric acid.

Another cause is the action which the acids themselves exert upon glass when they are in the state of vapour, and an action which is sometimes equal to that of hydrofluoric acid. This is proved by the following experiment, which can be easily made in a quarter of an hour. On a plate of glass covered with a layer of wax, a regular design is traced with a porcupine's quill; this plate is destined to cover a platinum crucible half-full of fuming sulphuric acid, and into which distilled water is poured so as to produce a considerable elevation of temperature. The aperture is closed by the glass plate, the outer surface of which is cooled by a stratum of water; when the temperature of the crucible falls, a fresh quantity of water is added, and so on until the addition of water causes no sensible evolution of heat. The operation is then completed; the wax is melted,

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the surface of the glass is well wiped with a rag, and the traced figures will appear in intaglio, and perfectly visible to the naked eye.

This result would lead one to suppose that there was a large quantity of hydrofluoric acid in the fuming sulphuric acid; but it is easy to prove that there is none, for if the fuming acid be neutralized so as to convert it into a sulphate, and this salt be acted upon by an acid capable of displacing hydrofluoric acid, the engraving produced is not more visible than if the displacing acid had acted alone, that is to say, it only appears by means of a slight layer of moisture such as is produced by condensed breath.

All acids in a state of vapour may act upon glass, and fix upon it designs first traced upon the layer of wax; aqueous vapour itself is capable of this. These effects take place even in presence of silica, which proves still more that hydrofluoric acid has nothing to do with it.

The author proposes to remedy these causes of error by employing instead of glass a plate of rock-crystal, which is not acted upon by any acid, except hydrofluoric.—*Comptes Rendus*, March 30, 1857, p. 679.

On the Separation of Strychnine from the Stomach of a Dog which had been poisoned therewith. *By* E. Prollius.

Some years ago, Rabourdin recommended chloroform for testing China bark for its amount of alkaloids. From this the author was induced to employ chloroform in recovering and detecting strychnine in the dead body of a dog; and he found this process so advantageous, that he recommends it particularly for the detection of this and some other poisons.

The experiment which the author made was as follows. The stomach of the dog, which died two days before the commencement of the investigation, was cut to pieces, and with its contents extracted twice in a glass flask upon the steam-bath, with in all 10 oz. of alcohol and 5 grs. of tartaric acid. The filtered extract was put into a porcelain dish covered with paper, and evaporated by the heat of a drying chamber, amounting on an average to 104° F., until after the lapse of forty-eight hours only half an ounce remained. This fluid residue was separated, by a moistened filter, from a fatty film which had formed upon it, and a slight excess of caustic ammonia was added to it; by this, however, no perceptible precipitate was produced, although, as afterwards appeared, a considerable quantity of strychnine was present. To separate this, 20 to 25 grs. of chloroform were added to the fluid, and the whole was strongly agitated. After standing for a short time, the chloroform settled to the bottom, with a strong, permanent, milky turbidity; it was freed from all mother-liquor by decantation and agitation with water, and then mixed with three times its quantity of alcohol, in order to obtain a clear solution, which by not evaporating too rapidly, like unmixed chloroform, would enable a regular formation of crystals to be obtained. This anticipated crystallization occurred in astonishing beauty when the solution had been left to evaporate for some hours

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in a watch-glass, accidentally exposed to the action of a powerful sun-light. A solution of the crystals in alcohol rendered red litmus-paper blue; they had the peculiar taste of strychnine; with bichromate of potash and sulphuric acid they gave the well-known deep blue coloration; they were soluble without residue in dilute acetic acid, and precipitable therefrom by ammonia—indications enough for the recognition of strychnine. To determine the weight, the watch-glass was weighed first with, and afterwards without the crystals; the difference was $\frac{1}{3}$ gr. The dog had received 2 grs. of strychnine.

The advantages of this process, according to the author, consist especially in the fact, that by it an alkaloid may be reproduced very easily, even in small quantity, from a poisoned substance, free from any colouring matter, and consequently readily crystallizable and recognizable, and also in that none of the subject under investigation is lost in any way, or rendered inapplicable to any further examination that may be necessary.—*Archiv der Pharm.*, lxxxix. p. 168.

New Method of detecting Iodine and Bromine.
By MM. O. Henry, Jun. *and* E. Humbert.

The authors employed this process with the view of determining the presence of iodine in the waters of Vichy, in which its existence was a matter of dispute. It presents great analogy with that recommended by them for detecting traces of hydrocyanic acid in cases of poisoning, and is applicable in all possible circumstances. In the case of a mineral water it is as follows:—

The water (or the more or less concentrated residue of its evaporation) is treated with acid nitrate of silver. The precipitate formed must contain the chlorine, bromine, and iodine of the water. It is washed and carefully dried. It is then intimately mixed with a little cyanide of silver and introduced into a tube, at one end of which it is fixed between two plugs of wadding or asbestos. A current of very dry chlorine is then passed slowly over the mixture, whilst the corresponding part of the tube is slightly heated. The iodine, bromine, and cyanogen are displaced, combine and condense in the colder parts in the form of a white crystalline ring of iodide and bromide of cyanogen. The tube is then closed at both ends, and may serve in case of need as a piece of evidence.

The physical and chemical properties of iodide and bromide of cyanogen do not allow them to be confounded with other compounds. The iodide sublimes at 113°, and the bromide at 59° F. This allows them to be separated mechanically by plunging the tube into water at 86° F. The iodide and bromide give the principal characteristic reactions of iodine and bromine.

Pure substances must be employed to furnish the chlorine required, and the apparatus should be set in action for some time before the commencement of the experiment. For this purpose, cyanide of silver alone is put into the tube; if no trace of iodide or bromide of cyanogen sublimes, the operation may be proceeded with.—*Comptes Rendus*, March 23, 1857, p. 634.

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THE CHEMICAL GAZETTE.

No. CCCLIII.—July 1, 1857.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Tantalic Acid and its Hydrate. *By* H. Rose.

When tantalic acid is prepared by the process of Berzelius from the tantalites of Finland, namely, by fusing the fine powder of the latter with bisulphate of potash, treating the fused mass with water, digesting the undissolved tantalic acid with sulphuret of ammonium, and then purifying it with muriatic acid, it usually still retains much tin, especially when it is prepared from the tantalite of Kimitto. To purify it completely from oxide of tin and tungstic acid, it must, when prepared in the above way, be fused with three times its quantity of a mixture of carbonate of soda and sulphur. The fused mass is lixiviated with water, and, after washing, the undissolved part is digested with a little muriatic acid. After calcination the tantalic acid is still combined with soda, from which it can only be separated by fusing it with bisulphate of potash or ammonia, and treating the fused mass with water.

After calcination, tantalic acid is white. During calcination it remains almost white, or only acquires a very slight yellowish tinge; when cool, it is as white as before it was heated.

When tantalic acid is combined with strong bases, especially with alkalies, it is not easy to free the calcined acid therefrom. This is effected in most cases by fusion with bisulphate of potash, in which it must dissolve completely at a red heat. But if the acid has previously been exposed to a long-continued and very high temperature, such as that of the porcelain furnace, a portion of it obstinately remains undissolved, and in this case the fusion must be repeated.

This method, however, cannot be employed where the amount of alkali in the tantalate is to be determined. The potash-salt must then be replaced by bisulphate of ammonia. In this, tantalic acid usually dissolves to form a clear syrup, which, when cold, remains clear not only for months, but even for years, which is characteristic of tantalic acid. The fusion with bisulphate of ammonia may be effected in a glass flask with a long neck, as it takes place at a temperature below a dull red heat; by this means less sulphuric acid is volatilized, and it can be better observed whether the tantalic acid is completely dissolved.

In his memoir, the author describes all the precautions and manipulations which are necessary to obtain tantalic acid perfectly

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pure by fusion with bisulphate of potash or ammonia, and at the same time, also, to determine the base combined with the tantalic acid.

The tantalic acid produced by the decomposition of perchloride of tantalum by water, is of a different density from that obtained by fusion with an alkaline bisulphate. Tantalic acid is obtained from the perchloride of a different consistency, according as the water is suddenly poured over the chloride, or the latter is exposed for a long time to the action of atmospheric air, or still more to its moisture, by which muriatic acid is very slowly evolved from it. In the former case a considerable elevation of temperature takes place; the perchloride hisses when it comes in contact with the water, and the tantalic acid separates in the amorphous state and of a glassy structure. In the second case, no elevation of temperature is produced in the treatment with water, and the separated tantalic acid has a distinctly crystalline structure under the microscope.

Tantalic acid is not quite insoluble in the muriatic acid which is produced by the decomposition of the perchloride. The tantalic acid may, however, be completely separated from this solution by ammonia. If an excess of muriatic acid be added to a dilute solution of an alkaline tantalate, the tantalic acid dissolves, forming an opalescent fluid. Dilute sulphuric acid precipitates tantalic acid from such a solution, especially when the whole is boiled, but the separation of the tantalic acid is not completely effected in this way. Nitric acid behaves like muriatic acid towards solutions of alkaline tantalates. Tantalic acid is thrown down from its alkaline solutions by phosphoric acid, but not by arsenic acid and arsenious acid.

Volatile organic acids, such as acetic and succinic acids, produce precipitates in solutions of the alkaline tantalates. Oxalic acid and binoxalate of potash produce no precipitate in it immediately, but do so after some time; it is, however, almost entirely dissolved by boiling with an excess of oxalic acid. Tartaric, racemic, and citric acids produce no precipitates; and in the presence of these acids tantalic acid is not thrown down by ammonia.

The precipitate produced by gallotannic acid, gallic acid, or tincture of galls, is characteristic of tantalic acid. No precipitate indeed is formed by these reagents in solutions of the alkaline tantalates; but when sulphuric or muriatic acid is added, a light yellow precipitate is thrown down. This precipitate is formed both when the tantalic acid has been almost entirely dissolved by an excess of muriatic acid, and when a thick white precipitate of tantalic acid has been produced by sulphuric or muriatic acid; the latter then acquires the same light yellow colour by the addition of tincture of galls. Non-volatile organic acids, tartaric, racemic, and citric acids, prevent the formation of this yellow precipitate.

An alkaline tantalate mixed with muriatic acid gives no blue colour with metallic zinc. Even after the addition of sulphuric acid only a very indistinct blue coloration is produced.

Tantalic acid may be obtained in very different states of density, upon which the author has already published. The density varies,

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especially according to the different temperatures to which the acid has been exposed, and the mode of preparation by which it has been obtained. If it has been prepared by fusion with bisulphate of potash and exposed to a red heat after complete washing and the removal of the sulphuric acid, it may be obtained of the lowest specific gravity ever exhibited by tantalic acid, namely, of 7·055 to 7·065. At the same time it presents so distinct a crystalline structure, that it may almost be recognized by the naked eye or with the lens, but at any rate always with the microscope. If this tantalic acid be exposed only for a short time to a white heat, it acquires the great density of 7·986, but still retains the crystalline structure which it possessed before ignition.

The amorphous tantalic acid obtained by the sudden treatment of the perchloride with water, exhibited a similar density to the crystalline acid, which was prepared from the perchloride by the long continued influence of moist air; the former had a density of 7·280, the latter of 7·284. Other quantities of tantalic acid obtained from the perchloride exhibited different densities, namely, 7·028, 7·039, 7·125, and 7·529, according as they had been exposed for a longer or shorter time to a moderate red heat. When these were exposed for six hours to a very fierce charcoal fire, they attained the high specific gravity of 7·851. When exposed to the heat of a porcelain furnace, the density diminished to 7·783.

To trace the increase of density by the elevation of temperature in amorphous tantalic acid prepared from the chloride, it was exposed to a charcoal fire constantly becoming stronger and more sustained. By this means it gradually attained the following densities: 7·274, 7·383, 7·529, 7·536, 7·914, and finally 7·944. It had acquired a distinct crystalline structure, which however it lost again when exposed to the heat of the porcelain furnace, when its density diminished to 7·652. Although the tantalic acid was not fused by the long-continued action of the porcelain furnace, it was brought into a state similar to that, for example, of fused garnet, which has a less specific gravity than the crystallized garnet which occurs in nature.

A tantalic acid of the greatest density was obtained, when the acid which had been exposed to the heat of a porcelain furnace was fused with bisulphate of potash, by which it again acquired a crystalline structure, and exposed a second time to the heat of the porcelain furnace. This time it did not lose its crystalline structure, but attained the high density of 8·257. It is possible that the heat of the porcelain furnace was not strong enough to destroy the crystalline structure and render it amorphous.

As tantalic acid is not one of the stronger acids, it combines with the strong bases in several proportions, and it is difficult to determine with certainty which of the compounds is to be called the neutral one.

Hydrated Tantalic Acid.—Such a weak base as water can only be combined with tantalic acid with a feeble affinity. The hydrate is consequently not always obtained of the same composition.

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Where hydrated tantalic acid is prepared by the decomposition of the perchloride with water or by fusion with bisulphate of potash, and the subsequent treatment of the fused mass with water and with ammonia, it certainly contains similar quantities of water in both cases, but it is distinguished essentially by one property. The hydrate prepared from the perchloride exhibits a very brilliant incandescence at a red heat, which the other does not.

The amount of water in the hydrate dried at 212° F., is different according to the length of time during which it was exposed to that temperature. In general, however, it may be assumed that the composition of the hydrate is essentially $2HO + 3TaO^2$.

Tantalic acid may be thrown down in the form of hydrate by weak acids from the solutions of alkaline tantalates, but it is then precipitated in combination with a little alkali, forming therewith an acid, insoluble salt. If the precipitation be effected by strong acids, these usually combine with the precipitated tantalic acid, and form a compound in which the tantalic acid acts as a base towards the strong acid, and from which the latter can only be separated by long washing, or by alkalies, or by ignition, if it be a volatile acid.

But if tantalic acid be precipitated by sulphurous acid gas from the solution of tantalate of soda, it contains neither sulphurous acid nor alkali. The precipitate, after drying, is slightly yellowish, and coarsely granular, and resembles dried white of eggs. It contains a similar quantity of water with the hydrate prepared in other ways. This hydrate, like that obtained from the perchloride, exhibits a strong luminosity when ignited.

Tantalic acid in its soluble salts, and that obtained from the perchloride, is therefore of a different modification from that which has been exposed to a high temperature by fusion with bisulphate of potash, and becomes converted into this, or another modification, by ignition.—*Bericht der Akad. der Wiss. zu Berlin*, 1857, p. 116.

Chemical Investigation of Cyclamen. (Part I. Cyclamine.)
By S. DE LUCA.

The root of the *Cyclamen** is a tuber of the form of an orbicular, flattened cake, brown externally and white internally, and furnished with blackish radicles. The plant is cultivated for its fine purplish flowers; its tuber contains a saccharine fermentescible matter, starch, gum, and acrid, irritant, and poisonous substances. The juice is acid, and possesses an extremely acrid and styptic taste. The present paper gives the mode of extraction of the poisonous principle of the tuber (*cyclamine*) and its principal properties.

Four kilogrammes of tubers of *Cyclamen europæum* were washed externally with distilled water, cut into small pieces, and put into a

* This tuber contains on an average 80 per cent. of water, and leaves about ½ per cent. of ashes. The latter, according to the analysis of Ubaldini, contain potash, soda, lime, magnesia, silica, chlorine, sulphuric acid, phosphoric acid, and oxide of iron, but no trace of manganese or alumina.

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large flask with four litres of rectified alcohol. The whole was left for forty-eight hours in a place sheltered from the light, and the alcohol was then decanted off. The same tubers were afterwards crushed in a mortar, and put into the same flask with three litres of alcohol; at the end of a month the alcohol was recovered by expression. The residue still retained a slight acrid taste; it was reduced to a paste, and placed in the same flask with two litres of alcohol. After a contact of twenty days, the alcohol was pressed out. The alcohol from these three treatments was combined, filtered, and the greater part of it was condensed by distillation on the water-bath. The residue thus obtained, which was of a gelatinous aspect, was evaporated to dryness on the water-bath in a porcelain capsule, without access of light, and afterwards exhausted in the cold by rectified alcohol.

The alcoholic solutions of these treatments, united and filtered, were placed in a capsule, and left to spontaneous evaporation for forty days, at the bottom of the cellars of the laboratory of the Collège de France. At the bottom of the capsule there was then deposited a whitish amorphous substance, in the form of small agglomerations. This was carefully collected, washed several times with cold alcohol, and dissolved in boiling alcohol. This solution always deposited the dissolved matter in the form of small amorphous agglomerations; it is the active matter of the tuber of *Cyclamen*, cyclamine; it is dried in the dark, *in vacuo*, over concentrated sulphuric acid.

Cyclamine is an amorphous, white, opake, inodorous, friable, light, neutral substance; when exposed to moist air, it increases in volume, and absorbs a great deal of water. In contact with cold water, it acquires a certain transparency, and the aspect of a very adhesive and viscous jelly; by the spontaneous evaporation of the cold alcoholic solution, it is deposited in small white amorphous agglomerations, which become brown by the direct action of light; it dissolves readily in cold water, and this solution, when agitated, produces an abundant froth like soap and water, and has also the singular property of coagulating like albumen, at a temperature of 140° to 167° F. On cooling, and standing for two or three days, the coagulated portion dissolves again in the mother-liquor, and may be again coagulated by heat; it contains no nitrogen, and dissolves in great proportion in alcohol, when slightly heated; it contains neither phosphorus nor sulphur, and when heated upon a slip of platinum leaves a bulky cinder, which burns completely without residue. Its aqueous solution is not coloured blue by iodine, even after coagulation by heat; it does not reduce potassio-tartrate of copper, and is not fermented by yeast.

Its aqueous solution readily absorbs vapour of bromine, and coagulates without colour, if the bromine be not in excess; chlorine acts in the same way. The action of synaptase, aided by a gentle heat (86° to 95° F.), decomposes it, producing glucose, which reduces potassio-tartrate of copper, and ferments with production of carbonic acid and alcohol; acetic acid dissolves it in the cold,

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and does not coagulate it with heat; muriatic acid dissolves it in the cold, and coagulates it at about 176° F. with production of glucose; concentrated sulphuric acid produces a yellow coloration with cyclamine, which afterwards becomes a permanent violet-red; this coloration disappears on the addition of an excess of water, with formation of a white precipitate; bichloride of mercury has no action in the cold upon the aqueous solution of cyclamine; gallic acid coagulates it; nitric acid attacks it even in the cold, giving origin to acid compounds which combine with alkalies; this acid, however, acts differently upon cyclamine, according to its state of concentration, and its action is rendered energetic by heat. With fused potash, cyclamine evolves hydrogen, and gives rise to a peculiar acid, which is but slightly soluble in water; the taste of cyclamine is manifested in a few moments, with a peculiar acridity, which particularly affects the throat; cyclamine dissolves by heat, without decomposition, in glycerine, in absolute alcohol, in wood-spirit, and in the alkalies; the alcohols also dissolve it in the cold, but in small quantity; æther, sulphuret of carbon, chloroform, turpentine, and the essential oils, do not dissolve it. Its analysis gave—

	I.	II.
C	54·55	54·54
H	9·11	9·12

The juice of the tubers introduced into the stomach of a rabbit in doses of 10 or even 20 grms. is not fatal; pigs eat the tubers without inconvenience. The juice acts as a poison upon small fishes in a large quantity of water (1 cub. cent. of juice in 2 to 3 litres of water).

M. Bernard made some experiments, by injecting the juice furnished to him by the author, into the lungs and the areolar tissue, to see whether the active matter had any analogy with curari. The juice had been expressed three days. I. He injected 2 grms. into the crop of a large greenfinch, which died very quickly. II. 4 grms. into the trachea of a rabbit, which died in ten minutes in convulsions. III. 1 grm. of the liquid introduced under the skin of a greenfinch, caused death in twenty minutes, with convulsions. IV. 2 grms. of the solution, under the skin of a frog, caused death in half an hour: the heart no longer beat, the nerves and muscles were very slightly excitable, the intestines were considerably inflated and distended with gases.

These experiments show that the active matter of the tuber of *Cyclamen* acts upon the animal œconomy nearly in the same way as curari, but less energetically. The aqueous solution of cyclamine acts in the same way. The poisonous action is nearly neutralized by bromine. The following experiments were made by M. Bernard:—I. 1 cub. cent. of an aqueous solution of cyclamine was introduced under the skin of a frog; it died in five minutes. II. A second frog, treated in the same way, but with a solution saturated with vapour of bromine, died in three hours and a half. III. 2 cub. cent. of juice of *Cyclamen* under the skin of another frog, caused

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death, with convulsions, in twenty minutes. IV. The same quantity of juice, saturated with vapours of bromine, caused death in four hours.

In its property of coagulating by heat, cyclamine resembles albumen; in the mode of deposition from its alcoholic solutions, it approaches mannite; in the character of frothing, when its aqueous solution is agitated, it appears to be analogous to saponine; from its solubility in water after coagulation, it might be confounded with some organic salts of lime; in its action upon the animal œconomy, it behaves like curari; and in its decompositions, it presents the characters of salicine and populine. The aqueous solution observed with M. Biot's apparatus exhibited a weak rotatory power to the left.—*Comptes Rendus*, 6th April, 1857, p. 723.

Note on the Chromates of Lime and Strontia. *By* J. W. Slater.

Chemists are at variance as regards the solubility of the chromates of lime and strontia. In Rose, we find that the "chromate and bichromate of potash do not produce any precipitate in solutions of lime-salts," a statement which calls forth no remark either from his English or his French editor. Further, he declares that the bichromate gives no precipitate in salts of strontia. Gmelin, in his 'Handbook of Chemistry,' states that the chromates of potash give no precipitate even in the most concentrated lime solutions, whilst in a subsequent volume he directs chromate of lime to be prepared by precipitating chloride of calcium with chromate of potash. The behaviour of the chromates has been proposed as a means of distinguishing the three alkaline earths, baryta being supposed to be precipitated by both neutral and acid chromates, strontia by the neutral alone, and lime by neither. I find, however, that with the exception of the sulphate, all soluble salts of lime (lime-water included) are precipitated by the neutral chromate of potash, if the solutions are tolerably concentrated, and especially if heat be applied. Magnesia is not thrown down by chromate of potash under any circumstance, not even in presence of alcohol, which greatly promotes the precipitation of lime.

Concentrated solutions of the nitrate of strontia give a slight precipitate with the bichromate of potash.

Sheffield, June 24th, 1857.

Experiments on Urea and the Urates. *By* M. Gallois.

In 1848, Wöhler and Frerichs announced that urea introduced into the digestive passages was found unaltered in the urine, but this has been denied by other distinguished observers. To throw light upon this question, the author has made some experiments upon animals.

He made choice of the rabbit, as its urine normally contains but little urea, so that the detection of the urea administered would be facilitated. The rabbits were fed upon carrots throughout the course of the experiments.

He first ascertained as exactly as possible (by Millon's process)

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the normal proportion of urea in the urine of the rabbit in 24 hours; then, in a first series of experiments, 5 grms. of urea were daily injected into the stomach for three successive days, and in a second series, 5 grms. daily were also injected for three days.

In the first case, the author collected the urine once in the day, and easily ascertained that *the urea injected into the stomach of rabbits* passes unaltered into their urine in considerable quantity.

In the second case, he collected the urine in fractions, to see how long it was before the urea appeared in the secretion, and at what period the kidneys ceased eliminating it. He found *that the elimination of the urea is clearly perceptible in half an hour or forty minutes, and that it ceases in from sixty to seventy hours, whatever may be the quantity of urea injected.*

On the Poisonous Action of Urea.—The deleterious action of urea upon the living organism is not mentioned in any treatise on Toxicology. It is, however, a very active poison to rabbits. Authors are contented with saying, that when urea accumulates in the blood, it determines, in consequence of its conversion into carbonate of ammonia, a series of symptoms which constitute urema. The author considers this last opinion by no means incontestable.

He administered doses of 20 grms. of urea to five rabbits, the weight of which varied between 1500 and 2000 grms.; they all died with the same symptoms. The symptoms of poisoning by urea in rabbits are,—acceleration of respiration, weakness of the members, tremblings with starts, general convulsions, then tetanus and death. Natural urea poisons rabbits exactly in the same way as artificial urea, so that death cannot be imputed to cyanides which might be contained in artificial urea; these bodies could not be detected in the urea employed by the author. The author also concludes from his experiments that the urea acts as a poison of itself, and not by conversion into carbonate of ammonia; he could not detect carbonate of ammonia in the air expired by the animals.

According to Wöhler and Frerichs, uric acid introduced into the œconomy would contribute to the formation of mulberry calculi, by becoming converted into oxalic acid, urea, and allantoïne. They did not find allantoïne, but state that they ascertained the production of oxalic acid and urea. The author found that the proportion of urea was not increased in the urine of a rabbit, into the stomach of which he injected first 2·50 gr., and a second time 7·30 gr. of urate of potash. On the contrary, it appeared less than before the administration of the urate, and he supposes that the opposite result obtained by Wöhler and Frerichs is due to their having probably analysed the urine of some particular emission, instead of that of 24 hours. With the microscope no oxalate of lime was detected in this urine; nor did the author find this salt in the urine of a dog, into the jugular vein of which he injected at twice 3 grms. of urate of ammonia. Lastly, he made two experiments on himself:—the first time he swallowed 5 grms. of urate of potash, and the second time 4·10 gr. After the first ingestion he found numerous crystals of oxalate of lime in his urine; after the second there were none.

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From these experiments, the author concludes that there is probably a relation between the uric and oxalic diatheses. But uric acid, in becoming oxidized in the organism, does not always furnish urea, allantoïne, and oxalic acid. Without taking into account the intermediate products, which appear to be variable, oxalic acid seems actually to be a product of the combustion of uric acid in the œconomy, and by combining with ammonia, it may, by subsequent reactions, give rise to oxalate of lime.—*Comptes Rendus*, April 6, 1857, p. 734.

On the Employment of Ferrocyanide of Potassium for the removal of Rust-Spots in White Linen. *By* Professor Runge.

The employment of ferrocyanide of potassium may often help us out of great difficulties in the case of rust-spots in linen. These do not always consist of common hydrated oxide of iron, but also frequently of oleate of iron, which can only be removed with difficulty, and with the assistance of heat, by oxalic acid, or the binoxalate of potash; and often not at all by sulphuric or muriatic acid, for these acids can only be applied cold and very dilute, as otherwise the linen suffers. From the high price of oxalic acid, therefore, a cheap means is wanting, when a great quantity of such iron moulds is to be destroyed. A case of this kind once occurred to the author, in which sulphate of iron had been used instead of potash, by which 300 napkins and other table-linen all acquired a rusty yellow colour, which, on being washed with soap, instead of disappearing, became darker; the sulphate of iron being decomposed by the soap, and oleate of iron precipitated upon the fibres.

Immersion even for several days in water acidulated with sulphuric and muriatic acids produced no effect, because the oleate of iron was not decomposed. It was here that the ferrocyanide of potassium did such excellent service. It was added in comparatively small quantity to the water, acidulated with sulphuric acid, and the linen was then moved about in the fluid. The linen became blue. When all the yellow had disappeared, and a clear blue had made its appearance, the linen was rinsed and treated with solution of carbonate of potash. Here the blue colour again disappeared, and with it a great part of the yellow, which only remained in spots. These were then very easily got rid of by dilute sulphuric acid alone.

The explanation of this process is easy. By the formation of prussian blue, the oleic acid is separated from the oxide of iron. The carbonate of potash then brought into action combines with the oleic acid, decomposes the prussian blue, and at the same time also dissolves the greater part of the oxide of iron, so that almost all the iron-mould disappears from the stuff simultaneously with the prussian blue. Caustic lye does not act in the same way; it certainly destroys the blue, but the rusty yellow remains, because it has not the same solvent action upon oxide of iron as carbonate of potash.—*Polyt. Centralbl.* 1857, p. 542.

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*Researches on the Ammonia-cobalt Bases**.*

By WOLCOTT GIBBS *and* F. A. GENTH.

[Continued from page 194.]

Chloroplatinate of Purpureocobalt.—When a solution of bichloride of platinum is added to one of the chloride of purpureocobalt, a brown-red precipitate is thrown down, which is a combination of the two chlorides. When dried it has a fine rich brown-red colour and high lustre. The crystals seen under the microscope are usually aggregations of flat pale reddish-brown needles. They are very distinctly dichrous, the ordinary image being pale violet-rose, while the extraordinary image is rich orange-red.

The chloroplatinate is nearly insoluble in cold, and with great difficulty soluble in hot water. It resists the action of reducing agents much more powerfully than the chloroplatinates of the alkaline metals. Thus it must be boiled for a very long time with zinc and hydrochloric acid before a complete reduction of the platinum is effected. If the process be interrupted before the reduction is complete, brilliant yellow granular crystals are often formed in the liquid. We have not determined the constitution of these crystals, but they are not chloroplatinate of ammonium. Sulphurous acid reduces this double chloride readily, and yields a red solution containing the protochlorides of platinum and of cobalt. We may here remark, that so far as our observation has hitherto extended, the action of a reducing agent upon any constituent of a compound containing an ammonia-cobalt base extends invariably to the ammonia-cobalt base itself.

The chloroplatinate of purpureocobalt has the formula $5NH^3 . Co^2 Cl^3 + 2PtCl^2$, which requires

	Equivs.	Calculated.	Found.
Cobalt	2	10·10	9·93
Platinum	2	33·50	33·51
Chlorine	7	42·01	41·80

This salt is identical with the chloroplatinate described and analyzed by Claudet, and for which that chemist found the same formula, with the exception of the hydrogen, which he makes 16 in place of 15 equivalents. We have also obtained it from a chloride which gave the reactions of chloride of roseocobalt, but we must leave it for the present undecided whether in this case there was a conversion of roseocobalt into the isomeric purpureocobalt, by the action of the chloride of platinum, or whether the chloride of roseocobalt had already undergone the change. We consider it certain that the salt in question is a salt of purpureocobalt, because it contains *two* in place of *three* equivalents of bichloride of platinum. We shall show further on, that the oxygen salts of this base contain either *two* or *four* equivalents of acid, and it is well known that in the

* These researches form part of the 9th volume of the Smithsonian Contributions to Knowledge, and are accompanied in the original by a large number of woodcuts and measurements of crystals by Prof. Dana.—ED. CHEM. GAZ.

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chloroplatinates there is—we believe invariably—but one equivalent of bichloride of platinum for each equivalent of chlorine in the chloride with which it is united. Since there are three equivalents of chlorine in this chloride of purpureocobalt, we infer that two of them are differently combined from the other two, so that the rational formula of the chloroplatinate is

$$5NH^3 . Co^2Cl . Cl^2 + 2PtCl^2.$$

We shall develope this view more fully when speaking of the oxygen salts of purpureocobalt.

Oxalate of Purpureocobalt.—This most beautiful salt is readily prepared by adding a solution of oxalate of ammonia to one of chloride of purpureocobalt. After a short time violet-red needles are thrown down, which may be washed with cold water. As thus prepared, the salt is almost chemically pure. The colour of the oxalate of purpureocobalt is the violet $\frac{6}{10}$ of the first circle of Chevreul's scale; the crystals are not sensibly dichrous. We have not, as yet, obtained measurable crystals of this salt. Under the microscope four- and six-sided acicular prisms are distinguishable, but without characterizing terminal planes.

The oxalate of pupureocobalt has the formula $5NH^3 . Co^2 O^3, 2C^2O^3 + 3HO$, which requires

	Equivs.	Calculated.	Found.	
Cobalt.....	2	22·09	22·00	21·95
Oxalic acid....	2	26·96	27·11	——

The oxalate is nearly insoluble in cold water, and not very soluble in boiling water, even after addition of free oxalic acid. The salt does not crystallize well from its solutions, and we have always obtained it in the most beautiful form by direct precipitation from the chloride. The salt is neutral to test paper, and is the only neutral oxysalt of purpureocobalt which we have yet obtained. It will appear from what follows, extremely probable that there is an acid oxalate of purpureocobalt containing 4 equivalents of oxalic acid. We have not obtained such a salt, however, in one or two experiments made for the purpose.

Acid Sulphate of Purpureocobalt.—Our efforts to obtain a neutral sulphate of purpureocobalt containing 2 equivalents only of sulphuric acid have hitherto been fruitless. When a solution of chloride of purpureocobalt is treated with sulphate of silver, chloride of silver is formed, and the red supernatant liquid yields, on evaporation, crystals of sulphate of roseocobalt. Precisely the same result is obtained with the chloride and nitrate of silver; the red solution yielding crystals of nitrate of roseocobalt. We consider it probable that in these cases the sulphate and nitrate of purpureocobalt, $5NH^3 . Co^2 O^3, 2SO^3$, and $5NH^3 . Co^2 O^3, 2NO^5$, are really formed by double decomposition, but that during evaporation the equivalent of free sulphuric or nitric acid formed at the same time with the sulphate or nitrate, reacts upon this so as to convert it into a salt of

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roseocobalt with three equivalents of acid. In equations we should have for the sulphate

$$5NH^3 . Co^2 Cl^3 + 3AgO, SO^3 + HO = 5NH^3 . CO^2 O^3, 2SO^3 + HO, SO^3 + 3AgCl.$$

$$5NH^3 . CO^2 O^3, 2SO^3 + HO, SO^3 = 5NH^3 . Co^2 O^3, 3SO^3 + HO.$$

When oil of vitriol is poured upon chloride of purpureocobalt in quantity sufficient to make a thick paste, the mass assumes a fine purple colour, and swells up very much at first, so that a large vessel is necessary. If the solution, after the evolution of hydrochloric acid has ceased, be diluted with about twice its volume of water, and allowed to stand for a few hours, a large mass of beautiful violet-red needles is deposited. The mother-liquor, after standing for a longer time, deposits more crystals. These crystals are to be quickly washed with a little cold water, drained and dried by pressure between folds of bibulous paper. They are usually free from chlorine, and are very nearly pure acid sulphate of purpureocobalt. The mother-liquor contains more of the acid sulphate, together with small quantities of another sulphate which we shall describe more fully hereafter, and frequently a little undecomposed chloride. By boiling this mixture with hydrochloric acid chloride of pupureocobalt is formed, which may be employed in preparing a fresh portion of the acid sulphate.

The acid sulphate of purpureocobalt may also be prepared by the action of strong sulphuric acid upon the sulphate of roseocobalt. For this purpose oil of vitriol is to be poured upon the sulphate in quantity sufficient to produce an oily liquid on heating in a water bath. The digestion is to be continued for one or two hours, according to the quantity of salt employed, care being taken that no oxygen is evolved. The dark purple liquid is to be suffered to cool, diluted with an equal bulk of water, and allowed to crystallize.

The acid sulphate as thus obtained is difficult to purify. By dissolving it in a small quantity of hot water and evaporating it quickly, fine crystals may sometimes be obtained. When, however, the solution is evaporated slowly in the air, crystals of sulphate of roseocobalt are formed in abundance, while the mother-liquor contains free sulphuric acid. When a solution of the acid sulphate is neutralized with ammonia, and allowed to crystallize by slow evaporation, the sulphate of roseocobalt is also obtained, but by rapid evaporation dark-red, prismatic cristals are sometimes formed, which we have not yet obtained in sufficient quantity for a complete analysis. They may prove to be the neutral sulphate of purpureocobalt.

The acid sulphate of purpureocobalt crystallizes in fine, red, prismatic crystals, which, according to Prof. Dana, belong to the trimetric system, and are hemihedral.

The acid sulphate is very soluble in water, and has a distinct though not strongly acid taste. It reddens litmus, and expels carbonic acid from the carbonates.

The formula of this salt is $5NH^3 . Co^2 O^3, 4SO^3 + 5HO$, which requires—

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	Eqvs.	Calculated.	Found.	
Cobalt	2	15·81	15·82	15·86
Sulphuric acid	2	42·89	43·19	
Hydrogen	20	5·36	5·31	
Nitrogen	5	18·76	19·00	

The acid sulphate gives no precipitate with $3KCy, Co^2 Cy^3$, but only a fine red liquid, which on evaporation yields a red mass. Boiled with hydrochloric acid the sulphate yields the chloride of purpureocobalt, easily recognized by oxalate of ammonia, with which, however, the acid sulphate itself gives no precipitate. When precipitated with nitrate of baryta, the acid sulphate yields a red liquid which probably contains a nitrate of purpureocobalt, but which on evaporation gives crystals of nitrate of roseocobalt. It is well worthy of notice, that this red liquid contains a large quantity of sulphate of baryta in solution, which it deposits during evaporation.

The products of the decomposition of the acid sulphate are similar to those of the other salts of purpureocobalt. A rapid current of NO^2 passed into the solution gives, after a short time, an abundant precipitate of the nitrate of xanthocobalt.

The constitution of the acid sulphate might be represented by either of the following formulæ, besides that already given:—

$$5NH^3 . Co^2 O^3, 3SO^3 + HO, SO^3 + 4HO.$$
$$5NH^3 . Co^2 O^3, 2SO^3 + 2HO, SO^3 + 3HO.$$

We reject the first of these formulæ, because purpureocobalt is a biacid and not a triacid base. The second formula appears to us less probable than that which we have adopted; in the first place, because a salt so constituted ought to be strongly acid, and in the second place, because we shall presently show that there exists an oxalo-sulphate of purpureocobalt, in which *two* equivalents of sulphuric are replaced by *two* of oxalic acid, and another and neutral oxalo-sulphate in which one equivalent of oxalic acid replaces one equivalent of sulphuric acid.

Acid Oxalo-Sulphate of Purpureocobalt.—When sulphate of roseocobalt is boiled for several hours with an excess of a solution of oxalic acid, a clear red solution is formed, which on evaporation deposits an abundance of crystals of a bright brick-red colour, and indistinct acicular form. These crystals are soluble in hot water without decomposition, and may be purified, though with difficulty, by recrystallization. Their constitution is represented by the formula $5NH^3 . Co^2 O^3, 2SO^3, 2C^2 O^3 + 5HO$, which requires—

	Eqvs.	Calculated.	Found.	
Cobalt	2	17·00	16·97	
Sulphuric acid	2	23·05	23·49	23·50
Oxalic acid ..	2	20·74	20·88	
Nitrogen	5	20·17	19·78	

The reactions of this remarkable salt resemble closely those of the acid sulphate. It has an acid taste and reaction, gives no precipi-

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tate with oxalate of ammonia or cobalticyanide of potassium, and yields chloride of purpureocobalt by boiling with an excess of hydrochloric acid. The formula of this salt may be written in various ways. In the first place, we may consider it as a double salt represented by the formula—

$$5NH^3 . Co^2 O^3, 4SO^3 + 5NH^3 . Co^2 O^3, 4C^2 O^3 + 6HO.$$

The advantage of simplicity is evidently in favour of the formula we have adopted. We may also consider it as represented by

$$5NH^3 . Co^2 O^3, 2SO^3 + 2C^2 O^3, HO + HO.$$

In this case the salt should have a strongly acid taste, which it has not. On the whole, the formula

$$5NH^3 . Co^2 O^3 \left\{ \begin{matrix} 2SO^3 \\ 2C^2 O^3 \end{matrix} \right. + 3HO$$

appears to deserve the preference.

Neutral Oxalo-Sulphate of Purpureocobalt.—When ammonia is added to a solution of the acid oxalo-sulphate just described, a fine violet-red colour is produced, and if no more ammonia be added than is sufficient to completely neutralize the acid reaction, the liquid yields, on evaporation, beautiful red prismatic crystals of a neutral salt. The neutral oxalo-sulphate is much less soluble in water than the acid salt, and has a purely saline taste: it is easily decomposed by boiling. The formation of this salt is represented by the equation—

$$5NH^3 . Co^2 O^3, 2SO^3, 2C^2 O^3 + 2NH^4O = 5NH^3 . Co^2 O^3, SO^3, + C^2O^3\ NH^4O, SO^3 + NH^4O, C^2 O^3.$$

The fact that the ammonia unites with both sulphuric and oxalic acid, and not simply with *two* equivalents of oxalic acid, throws much light on the constitution of the acid oxalo-sulphate, and shows, we think, clearly that the formula of this salt cannot be—

$$5NH^3 . Co^2O^3, 2SO^3 + 2C^2O^3, HO + HO.$$

The constitution of the neutral oxalo-sulphate is represented by the formula—

$$5NH^3 . Co^2 O^3, \left\{ \begin{matrix} SO^3 \\ C^2 O^3 \end{matrix} \right. + 7HO,$$

which requires—

	Eqvs.	Calculated.	Found.
Cobalt.....	2	19·21	19·23
Sulphuric acid	1	13·02	13·12
Oxalic acid....	1	11·72	
Nitrogen.....	5	22·80	22·83

We may further remark, that the character of the action of ammonia upon the acid oxalo-sulphate leads us to hope that the neutral sulphate of purpureocobalt may be obtained by the action of this agent upon the acid sulphate, and that, in fact, this is the salt already mentioned as so obtained, but not yet analysed. The two oxalo-sulphates described constitute, we believe, the types of an entirely

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new class of salts, and lead to the idea that sulphuric and oxalic acids may possibly be capable of replacing each other in combinations.

Oxide of Purpureocobalt.—The oxide of purpureocobalt, like that of roseocobalt, appears to exist only in solution. It may be prepared, either by decomposing the acid sulphate by baryta water, or by digesting a solution of the chloride with oxide of silver in the cold. The solution is not pure in either case, containing either sulphate of baryta or chloride of silver in solution. The oxide, as thus prepared in solution, forms a violet-red liquid, which absorbs carbonic acid readily from the air, and which is decomposed by concentration.

The constitution of the oxygen salts of purpureocobalt, which we have described, as well as that of the chloroplatinate of this radical, appears to us to leave no reasonable doubt that the oxide is essentially *biacid*. According to the rule that the number of equivalents of acid in a salt is equal to the number of equivalents of oxygen in the base, the rational constitution of the oxide of purpureocobalt will be expressed by the formula $5NH^3 . Co^2O . O^2$.

We shall develope this view more fully when occupied with the purely theoretical portion of the subject, and in the second part of our memoir we shall endeavour, by the analysis and description of other salts of purpureocobalt, to throw more light upon the nature of this remarkable radical. The chromates, pyrophosphates, and picrate of purpureocobalt have, in particular, occupied our attention.

We have mentioned, in speaking of the reactions of chloride of purpureocobalt, that both the cobalticyanide and the ferricyanide of potassium give precipitates in its solution. The constitution, crystalline form and physical appearance of these two precipitates exactly agree with those of the cobalticyanide and ferricyanide of roseocobalt, and we have therefore not hesitated to identify them with these last. We believe that in this case there is a conversion of purpureocobalt into roseocobalt, since in the salts in question there are 3 equivalents of cyanogen in the electro-positive for 3 in the electro-negative cyanide, the formula being as mentioned above,

$$5NH^3 . Co^2 Cy^3 + Co^2 Cy^3 + 3HO, \text{ and } 5NH^3 . Co^2 Cy^3 + Fe^2 Cy^3 + 3HO.$$

As purpureocobalt is certainly biacid, its cobalticyanide and ferricyanide should have the formulæ

$$3(5NH^3 . Co^2 Cy^3) + 2Co^2 Cy^3, \text{ and } 3(5NH^3 . Co^2 Cy^3) + 2Fe^2 Cy^3,$$

although the frequent occurrence of basic double cyanides may render this point less clear than the others, which also involve the biacid character of the radical.

[To be continued.]

On the Conversion of Mannite and Glycerine into a True Sugar. By M. Berthelot.

The analogies existing between the alcoholic fermentation of mannite and glycerine and that of the true sugars, at once give rise

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to the opinion that these two fermentations might not really be distinct; if mannite and glycerine furnish alcohol, they probably pass previously through the state of sugar.

To determine this question, the author has made various experiments, the results of which differed according to circumstances. Under the normal conditions of the alcoholic fermentation of mannite and glycerine, with the simultaneous influence of carbonate of lime and caseine, their conversion into alcohol, either at 104° F. or at 50° F., takes place directly, without the least indication at any moment of the temporary existence of a true sugar. But the regular course of these experiments requires the presence of carbonate of lime; if this be suppressed, the mannite and glycerine usually remain unaltered, but sometimes, and only under peculiar circumstances, the formation of a true sugar may be observed.

Mannite and glycerine dissolved in water were left at the ordinary temperature in contact with all the nitrogenous tissues and substances of an animal or analogous nature which the author could procure. In many cases a true sugar was produced, capable of reducing potassio-tartrate of copper, and of undergoing alcoholic fermentation under the influence of yeast.

The conditions of this formation of sugar are sometimes capable of definition, sometimes exceptional. It was observed with albumen, caseine*, fibrine, gelatine, and cutaneous, renal, and pancreatic tissues, &c., but always accidentally, and so that the conditions of the phænomenon could not be determined.

The tissue of the testicle alone caused the conversion of glycerine and mannite into true sugar almost in a regular manner. The testicles of man or animals (the cock, dog, or horse) are cut into small pieces and placed in a solution consisting of 10 parts of water and 1 part of mannite or glycerine; the weight of the animal tissue (supposed to be dry) should represent about $\frac{1}{20}$th of that of the mannite or glycerine. The operation is effected in an open bottle, under the influence of diffused light, at a temperature between 50° and 68° F. The tissue usually remains without putrifying; if it putrifies the experiment is a failure. The formation of moulds, and especially of *Penicillum glaucum*, is also injurious. After an interval of from a single week to three months, it is usually found that a substance has made its appearance capable of reducing potassio-tartrate of copper, and fermenting immediately with yeast. At this moment the fragments of testicle are separated by decantation, and completely freed from the mannite or glycerine by re-

* The following are some causes of error which must be well guarded against in these experiments:—1. Albumen and caseine contain small quantities of sugar, of which they must be freed. 2. The mannite of commerce must always be purified, as it contains 1 to 2 per cent. of sugar. This sugar is derived from the manna, which contains 10 to 15 per cent. The amount of sugar pre-existing in manna does not increase by keeping. Besides sugar and mannite, manna contains nearly half its weight of little known substances, so that the employment of manna in these experiments cannot lead to any conclusion. 3. The so-called *purified* commercial glycerine contains a body capable of reducing tartrate of copper.

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peated washing; in this state they possess the property of converting these two substances into true sugar. The prepared tissues are operated with in the way just described, and it is even sufficient to impregnate the tissue with a solution of mannite or glycerine, to obtain a very abundant formation of sugar in a few weeks. Some experiments made with dulcine gave similar results.

The sugar thus formed is analogous to glucose in most of its properties. It could not be obtained crystallized, and is very soluble in water, aqueous alcohol and glycerine, from which it can hardly be separated. It is a very hygrometric body, very alterable during the evaporation of its solutions, capable of becoming brown under the influence of alkalies, and of reducing potassio-tartrate of copper; ammoniacal acetate of lead does not precipitate it in sensible proportions. With yeast it ferments immediately, producing alcohol and carbonic acid. It was difficult to ascertain whether it possessed a rotatory power, from the readiness with which it becomes coloured during the concentration of its solutions. Once the author succeeded in observing a deviation of the tint of passage equal to 5°·5 for a length of 200 millims.; with a liquid containing about one-twentieth of sugar; it would therefore have a left-handed rotation, and be distinct from glucose and most of the other sugars in the direction of its rotatory power.

One of the most decisive of the author's experiments to determine the origin of this substance and the influence of the testicular tissue upon its formation, is as follows:—

On the 18th of December, 1856, he weighed 2 grammes of fresh cock's testicles (representing 0·280 grm. in the dry state), 5 grms. of mannite, and 50 grms. of water; the whole was put into a bottle communicating with the atmosphere through a tube filled with carded cotton, and left in a moderately heated laboratory. On the 12th of April, 1857, the liquid contained 0·250 grm. of true sugar. The fragments of testicle retained their form and microscopic appearance; some almost inappreciable traces of vegetation were discovered on careful examination. When washed and dried, these fragments weighed 0·230 grm., so that they had lost 0·050 grm. This loss, however, is rather apparent than real, for the fresh testicles contain a certain portion of saline and other substances which are soluble in water, and a portion of the tissue becomes disaggregated and soluble without changing into sugar; all these products are calculated as loss, although they are found in a soluble state, and partially coagulable during the evaporation of the liquid. Taking into account these various circumstances, and the proportion of sugar formed in the preceding and other experiments, without speaking of the analogies of composition and constitution existing between the sugars and mannite and glycerine, we shall be led to regard the sugar thus produced as resulting principally, perhaps exclusively, from the transformation of the mannite or glycerine. This conclusion is also confirmed by other experiments, in which, without perceptible diminution, the testicular tissue produced the conversion of mannite into sugar, seven times consecutively.

These facts tend to assimilate the influence of the testicular

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tissue with the actions of contact which have been observed in inorganic chemistry, and this is confirmed by the permanence of the microscopic structure of the tissue in the course of the experiments. These, however, are probabilities rather than a demonstration. In fact, the animal tissues do not enjoy that absolute invariability of composition which often characterizes the mineral compounds acting by contact. At the same time that the tissue acts, it becomes continuously altered; it is decomposed without putrefaction, as shown by analysis.

Thus it cannot be decided positively whether the tissue operates by the action of contact in virtue of its organic structure, or its chemical composition, or whether the very fact of its decomposition does not exert some influence. Lastly, the contact of the air, without which these experiments would not succeed, introduces a new complication, for it allows the development of microscopic animal vegetable organisms; this could never be altogether avoided, but it appears rather injurious than otherwise. In the most successful experiments, the formation of organized beings took place in the lowest possible degree.

These details show how complex are the phænomena of fermentation, and how many unknown and obscure elements they include; nevertheless, chemists may set in action the forces which cause them, and direct them upon definite bodies, and to the accomplishment of determinate metamorphoses. It is nearly in the same way that they set in action the ordinary affinities, the intimate nature of which is scarcely better known. The employment of ferments is only distinguished therefrom by the pre-existence of a peculiar and extremely mobile form and constitution, produced without one intervention, under the influence of life.

However this may be, the preceding experiments are distinguished by their synthetic character from the fermentations hitherto known. Instead of changing sugar, mannite, or glycerine into alcohol, lactic and butyric acids, more simple compounds, and more difficult of decomposition, they lead to the conversion of mannite and glycerine, bodies which are tolerably stable, deprived of rotatory power, and approaching those which we know how to produce, into a substance endowed with less stability and of a higher order of complication, in fact, into a true sugar, analogous to those formed under the vital influence in the interior of the vegetable and animal tissues. *Comptes Rendus*, May 11, 1857, p. 1002.

ANALYTICAL CHEMISTRY.

On Testing the Amount of Acetic Acid in Vinegar. *By* J. Otto.

Nicholson and Price* have brought the process of determining the amount of acid in vinegar by neutralization by alkalies or alkaline carbonates, into disrepute. They state, that very inaccurate results

* Chem. Gaz. 1856, p. 30.

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are obtained, because the alkaline acetate has an alkaline reaction; and that the testing must be effected with carbonate of lime or baryta, or by means of the carbonic acid apparatus of Fresenius and Will. They found these statements upon experiments, the results of which are summed up in what follows. The numbers indicate the per-centage of hydrated acetic acid, which was found by the various methods of testing in concentrated or dilute acetic acid.

Carbonate of soda.	Carbonate of lime.	Carbonate of baryta.	Fresenius & Will's Method.
87·9	99·6	99·4	99·3
45·3	52·8	52·3	52·0
22·1	25·5	25·7	25·3

How different are the numbers of the first series from the corresponding numbers in the others, in which the greatest accordance is exhibited!

The experiments of Nicholson and Price were exceedingly unwelcome to me, as I was just engaged in the preparation of a new edition of my Text-book of Vinegar Manufacture. I should have to condemn the former method in general use, for the determination of the amount of acid in vinegar, as well as my acetometer, in which a dilute ammonia is used as the acetometric fluid. Not so much to check the correctness of the experiments in question, which appeared to me to be beyond a doubt, as to see whether, in the case of an acetic acid so diluted as the vinegars, the error was not so small that it might be passed unnoticed, or whether it was not constant in amount, I made a few experiments. I will communicate these in the following. The numbers represent centesimal parts of anhydrous acetic acid in the vinegar examined.

Acetometer.	Carbonate of soda.	Carbonate of baryta.
6·3	6·5	6·2*
9·1	9·2	9·0

The acetometric ammoniacal fluid was prepared with the greatest exactitude.

For testing with carbonate of soda, a normal solution of the anhydrous salt containing 104 grms. in the litre was employed, and a Mohr's burette was used. 5 cub. cent. of the solution indicate 1 per cent. of acetic acid in 50 grms. of vinegar. The point of neutralization was ascertained in the heated vinegar by means of pale blue litmus paper.

In testing with carbonate of baryta, a weighed quantity of the salt was put into a weighed quantity (10 or 50 grms.) of vinegar, and digested therewith, at last at a high temperature, until the solution produced had an alkaline reaction. For this purpose a long time was required. The undissolved carbonate of baryta was collected on a filter, carefully washed, dried, calcined and weighed. 98·5 of carbonate of baryta, represented 51 of acetic acid (1 equiv.).

It might be objected against these experiments, that possibly I

* In two perfectly concordant experiments.

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did not continue the digestion of the vinegar with the carbonate of baryta long enough, for there is no other means of judging of the completion of the digestion, except the reaction. For this reason I made the following experiments, which must remove all doubt, and which may easily be repeated in a few minutes.

27 grms. of crystallized acetate of soda were dissolved to form 100 grms. of solution. This solution contained 10 grms., or 10 per cent. of acetic acid. It had an alkaline reaction with reddened litmus paper. It was rendered perfectly neutral by 2 cub. cent. of vinegar, containing 4·5 per cent. of acid, and the addition of 1 cub. cent. more vinegar caused it to react distinctly acid upon blue litmus paper; 2 cub. cent. of vinegar of 4·5 per cent. do not contain fully 0·1 grm. of acetic acid; the error, therefore, which results from the alkaline reaction of acetate of soda in the determination of the acidity of a vinegar of 10 per cent., can at the utmost only amount to $\frac{1}{10}$th per cent., and is certainly always less, as a little too much soda is usually added.

A hot solution, containing 50 per cent. of acetate of soda, representing 18·7 per cent. of acetic acid, was rendered neutral by 2 cub. cent. of vinegar of 9 per cent., and distinctly acid by another cub. cent.

The process hitherto in use for the determination of the amount of acid in vinegar by means of alkalies or alkaline carbonates may therefore be retained, as it gives sufficiently accurate results; the alkaline reaction of the alkaline acetates does not affect the accuracy in a noticeable degree.

When, many years ago, I constructed the acetometer to which my name has been given, and by means of which the amount of acid in a vinegar is ascertained very conveniently and rapidly, and also very exactly if the acetometric fluid has been correctly prepared, I was obliged to make experiments as to the amount of ammonia in liquid ammonia of various specific gravities, and sketch out a Table of them. Very recently, Carius has ascertained the amount of ammonia in solutions of ammonia in a very different way (Liebig's Annalen, xcix. p. 129). As appears from the following comparison, my Table agrees so closely with that calculated by Carius, that it deserves perfect confidence for use in the preparation of the acetometric fluid.

Amount of ammonia in the fluid.	Specific gravity.	
	Carius.	Otto.
12 per cent.	0·9520	0·9517
11 „	0·9556	0·9555
10 „	0·9593	0·9593
9 „	0·9631	0·9631
8 „	0·9670	0·9669
7 „	0·9709	0·9707
6 „	0·9749	0·9745
5 „	0·9790	0·9783

Liebig's *Annalen*, April 1857, p. 69

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THE CHEMICAL GAZETTE.

No. CCCLIV.—July 15, 1857.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On some Products of Decomposition of the so-called Proteine Compounds. *By* Dr. MÜHLHÄUSER.

In a previous memoir* the author described two products of decomposition which are formed by the action of fuming nitric and muriatic acids upon all proteine compounds. One (1) of these is the very volatile chlorazole which is obtained by the distillation of the albuminates thus treated. The other (2) is not volatile, and separates by this process as a clear, tenacious fluid mass in the residue of the retort.

In the mother-liquor of this latter mass we find oxalic acid, the constituents of the ash, the sulphur oxidized to sulphuric acid, (3) an oleaginous body, and (4) fumaric acid crystallizing in grains. These four bodies are essentially the products formed during the above-mentioned process.

The third and fourth bodies are obtained as follows. The fluid is evaporated from the tenacious mass, until the muriatic and nitric acids are for the most part driven off, if considerable quantities of them were still contained in it. After some time, sometimes not for several days, a crystallization of free oxalic acid takes place, and after the separation of this perhaps even a second crystallization of alkaline oxalates and free acid. If no further deposition takes place in the mother-liquor when further reduced, the thickish fluid is mixed with three or four times its volume of cold water. An aromatic odour is evolved, and the separation of the third body commences in fine brownish-red or dark-brown drops. The remaining mother-liquor is then again concentrated and left to stand for some days, when the fourth body makes its appearance in brown crystalline spheres at the surface and in similar crusts at the bottom of the dish. After two depositions of both bodies, the mother-liquor is nearly exhausted.

The third body is formed in about the same quantity as the first two; the amount of the fourth is much smaller, and only about one-fourth part of it. The quantity of oxalic acid, on the other hand, is usually equal to, and often greater than that of any of the first three bodies.

The oleaginous body, $C^{36}H^{18}Cl^3NO^{18}$, is of a deep brownish-red, when it is deposited from the mother-liquor; paler when the latter

* See Chem. Gaz. vol. xiii. p. 465.

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still contains nitric acid. It has a pleasant odour, is strongly aromatic, and has an acid reaction. It is readily soluble in alcohol, and dissolves in water rather more easily than the second body, with which it agrees in several properties.

It does not detonate when heated, its coal is readily combustible; in the cold it becomes opake and stiff. Analysis:—

C	35·52	35·14	35·4	26	=156	35·57
H	4·4	4·4	4·3	18	18	4·15
Cl	23·42	23·41	..	3	106·5	24·2
N	3·2	..	..	1	14	3·1
O	..	..	..	18	144	32·8

With bases this body gives no definite compounds adapted for the determination of its atomic weight. The precipitates with solution of silver are always amorphous, brown, partially soluble in water, and forming a jelly therewith; they soon become black and contain very unequal quantities of silver, and much more than corresponds with the atomic weight, which cannot be placed lower in accordance with the analyses, whilst there is rather reason for doubling it. The baryta compound, prepared by the addition of baryta-water to the alcoholic solution of the body, is also amorphous, brown, difficult of solution in water, and exhibits a slight detonation when ignited, which does not take place with the compounds with potash and soda, in which the body is readily soluble. Aqueous ammonia scarcely dissolves it, and does not combine with it; metallic salts furnish amorphous, strongly coloured precipitates. During the drying of all the compounds, a portion of the organic substance is volatilized.

The *fumaric acid* is much more easily obtained than the former products, as it separates by crystallization.

Products of decomposition of the two Non-volatile Products.—Only very energetic reagents are capable of further decomposing the two non-volatile bodies. The author treated them with fuming nitric acid. The products, amongst which no more oxalic acid makes its appearance, are as follow:—

A. The body to which the author in his former memoir attributed the formula $C^{24}H^{12}Cl^3NO^8$, indicated here by No. 2, when distilled with 100 times its quantity of fuming nitric acid (1·5), gives chlorazole (1) together with the excess of acid. This chlorazole has a different composition from that obtained directly from the proteinaceous bodies, corresponding with the formula $C^4H^2N^2Cl^2O^3$. Its properties, however, are similar. Analysis:—

C	12·03	12·78	4	=24	12·70
H	1·07	1·13	2	2	1·06
Cl	38·4	38·5	2	71	37·6
N	13·1	15·7	2	28	14·8
O	..	..	8	64	33·8

In the retort is formed (2) a crystalline body, which agrees most closely with bichlorosalicylic acid, but nevertheless exhibits differ-

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ences in its properties. Thus bichlorosalicylic acid is dissolved and decomposed by nitric acid with difficulty; this body, on the contrary, is readily soluble in hot nitric acid, and separates again therefrom without alteration, as indeed its mode of preparation shows. It combines readily with bases, and the alkaline salts are soluble in cold water. The soda-salt had the atomic weight 203·7. The potash-salt is reddish and crystalline; its atomic weight is 192·7. The precipitates given by the alkaline salts with solution of silver are amorphous and reddish-brown; in a dilute solution they become gelatinous and cannot be obtained crystalline; their composition is unstable. The silver compound contained 33 per cent. of silver; calculation requires 34·4 per cent. Its analysis gave,—

C	40·1	40·5	41·72	14 = 84		40·37
H	2·7	2·6	2·3	4	4	1·93
Cl	34·17	34·53	..	2	71	34·29
O	..	..	..	6	48	23·21

Lastly, there remains dissolved in the mother-liquor in the retort (3) an acid of the composition $C^{12} H^3 Cl^2 NO^6$, which has the greatest similarity to the original body from which it was produced. It is clear, thickly fluid, may be drawn out in threads when dry, is of a slight reddish-yellow colour, readily soluble in hot nitric acid, by which it is not further changed, and also in alcohol and æther, and difficult of solution in water. It has a strongly acid reaction, is inodorous, attracts water very greedily from the air, and when heated furnishes a vapour of a peculiar odour, which gives rise to coughing. It is volatilizable without alteration; when heated in tubes, it creeps up along the sides, without changing colour; and when evaporated leaves no coal. When heated it is not oxidized. Analysis:—

C	33·4	34·2	34·26	..	12 = 72		34·65
H	1·6	1·8	1·9	..	3	3	1·44
Cl	33·3	33·75	34·1	35·0	2	71	34·10
N	6·6	7·5	..	..	1	14	6·74
O	..	..	..	..	6	48	23·15

These numbers correspond with a chloronitrate of carbolic acid, in which 3 atoms of hydrogen are replaced by 2 atoms of chlorine and 1 atom of hyponitric acid, $C^{12} \left\{ \begin{matrix} H^3 \\ Cl^2 \\ NO^4 \end{matrix} \right\} O^2$. A body of similar composition, but of quite different properties, was obtained by Laurent from coal-tar oil which he treated with gaseous chlorine and afterwards with nitric acid. This, however, is crystalline and explosive, and resembles picric acid both in itself and in its salts.

B. The body here indicated by No. 3, of the composition $C^{26} H^{18} Cl^3 NO^{18}$, furnishes very similar but not exactly the same products by similar treatment with fuming nitric acid.

1. The chlorazole formed has the same properties as that previously obtained by the author. Its analysis gave,—

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C	13·05	13·2	4=24		12·6
H	0·7	0·8	1	1	0·52
Cl	36·8	..	2	71	37·36
N	7·8	..	1	14	7·3
O	..	..	10	80	

These numbers differ from those previously obtained.

2. In this case also a crystalline body is produced, which nearly approaches the similar product from the preceding body, but has a different crystalline form and composition. It is perfectly inodorous, and more difficult of solution in hot water. It is readily soluble in alcohol, when it has an acid reaction, and crystallizes from the solution in white, short, very fine needles, grouped in a stellate form. It fuses when heated, when a vapour of a different, agreeable odour, but not similar to that of aromatic bodies, provocative of coughing, is evolved; it sublimes readily and in the same form, in microscopic, usually broad needles, with oblique terminations; it is then extremely light. Its analysis gave,—

C	45·8	46·1	45·1	16=96		46·8
H	3·05	3·03	..	6	6	2·9
Cl	34·42	33·75	36·51	2	71	34·6
O	..	..	..	4	32	15·6

3. In the nitric acid from which Nos. 1 and 2 were separated, an oleaginous body remains dissolved; it is obtained, when the acid is distilled off, by the addition of water and heating. This body is clear and pale-yellow, has rather more consistence than the body from which it is derived, is almost inodorous, of a bitter taste, and strongly acid reaction; it is readily soluble in alcohol, sparingly in water, and possesses the general properties of the similar body already described. It is, however, volatile, and may be sublimed in white vapours which condense in the previous form; at the same time it evolves a peculiar odour, different from that of the body from which it is derived, but similar to that of the corresponding member of the first decomposition, from which, however, it is essentially different in its composition. Analysis:—

C	33·24	33·11	33·05	24=144		33·9
H	4·05	3·9	3·8	16	16	3·8
Cl	25·0	24·77	..	3	106·5	25·0
N	3·3	3·3	..	1	14	3·2
O	..	..	..	18	144	33·9

This body furnished no compounds which could serve for the establishment of its atomic weight. The compounds are all amorphous, of a brownish-red or orange colour, and contain far more base than corresponds with the atomic weight; the same inconveniences are presented here as with the parent body itself.

It appears, therefore, essentially from the facts which the author has published in his two memoirs, that in the above-mentioned treat-

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ment two non-volatile chlorinated bodies make their appearance as the principal products in nearly equal quantities. They are formed in a similar period of the decomposition, possess a mutual resemblance, and break up into similar elements, which are simple and volatile, as the subsidiary products (oxalic acid) are from the first. Finally, we have a series of very different volatile bodies, the groupings of which we know. Three of these are elements of one, and three of the other volatile product; but these two, with chlorazole, fumaric acid, and sulphur, appear to constitute the yellow amorphous body soluble in alcohol, which is formed in this case at the very commencement, and approaches most closely to the proteinaceous bodies, but which has lost the greater part of its nitrogen and all its ashes, and is not identical with xanthoproteic acid.—Liebig's *Annalen*, ci. p. 171.

On the Compounds of Tantalic Acid with Potash. *By* H. Rose.

By fusion in hydrate of potash, tantalic acid dissolves into a clear fluid, and after cooling the fused mass is perfectly soluble in water. As, however, tantalate of potash is soluble in all proportions in hydrate of potash, and cannot be separated by crystallization from the solution, it is very difficult to prepare the salt in a pure state. If it be attempted to remove the excess of hydrate of potash by alcohol, the compound, $KO+2TaO^2$, which is the neutral salt, is certainly obtained, but mixed with carbonate of potash.

When tantalate of potash has been freed as much as possible from the excess of hydrate of potash by alcohol, it has lost its solubility in water, at least for the most part, and the portion that dissolves is thrown down from the solution when the latter is boiled for some time. The precipitated salt has essentially the composition $KO+6TaO^2$.

The same compound is also obtained when the neutral salt is repeatedly mixed with muriate of ammonia and ignited until no further loss of weight takes place, after which the chloride of potassium formed is separated from the acid tantalate of potash by water.

In the humid way, tantalic acid cannot expel carbonic acid from carbonate of potash. But if the acid be fused with carbonate of potash, the carbonic acid of the latter is readily driven off.

The author formerly laid great stress upon such experiments, in order to be able to determine with certainty the capacity of saturation of several fire-resisting acids. He has, however, since doubted greatly of the importance of the results which may be attained by these experiments; for the acids which are submitted to these experiments belong to the weaker acids, which are capable of combining in many proportions with the same strong base, so that more carbonic acid can always be driven out of the fused mass, when the temperature is raised.

In several experiments, when weighed quantities of tantalic acid and carbonate of potash were fused together, so much carbonic

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acid was driven out of the latter that the compound $5KO+4TaO^2$ must have been produced.

When larger quantities of tantalic acid are fused with carbonate of potash, and the fused mass is treated with water, the greater part of the tantalic acid remains undissolved as an acid salt, even when the temperature of the fusion has been high. The solution contains, besides tantalate of potash, much carbonate of potash; if it be evaporated, crystals are obtained which contain both salts; and the tantalate of potash contained in these may be regarded as a very basic salt of the composition $2KO+TaO^2$. The insoluble salt separated during the treatment with water is $KO+4TaO^2$. The longer this salt is boiled with water, the more tantalic acid does it contain; and it finally acquires the composition $KO+5TaO^2$. An exactly similar compound is obtained when carbonic acid gas is passed through a solution of neutral tantalate of potash.—*Bericht der Akad. der Wiss. zu Berlin*, 1857, p. 206.

On a New Double Salt of Bromide of Sodium and Bromate of Soda. *By* J. Fritzsche.

During the spontaneous evaporation of a fluid, obtained by the gradual introduction of bromine into a moderately concentrated solution of soda, prismatic crystals were formed which were sometimes obtained in larger, sometimes in smaller quantities. They are—

The double salt, $2NaBr+3(NaO\,BrO^5)+6HO$.—On being dissolved again in water it is decomposed into bromide of sodium and bromate of soda. It is also decomposed by alcohol. The crystals belong to the monoclinohedric system. Analysis gave:—

NaBr	28·26	2	=2578·70	28·904
NaO, BrO^5	61·66	3	5668·05	63·532
HO	8·73	6	674·88	7·564

Bull. St. Pétersb. xv. p. 274.

Researches on the Ammonia-cobalt Bases. *By* Wolcott Gibbs *and* F. A. Genth.

[Continued from page 255.]

Luteocobalt.

The salts of luteocobalt have a yellow or brown-yellow colour, and are almost always well crystallized. They are in general more soluble in water than the corresponding salts of roseocobalt; the solutions have a brown-yellow colour. The salts of luteocobalt are very stable in the presence of acids in general, but are decomposed by long heating with sulphuric acid. The neutral and alkaline solutions are readily decomposed by boiling, like the salts of the other cobalt bases. Nearly all of them a have purely saline taste. When hydrated, these salts generally effloresce in dry air or *in vacuo*, and become opake, with a peculiar porcelain-like lustre and reddish-buff

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colour. The salts of luteocobalt may be formed, like those of the other bases described, by direct oxidation; it is well worthy of notice, however, that they are often found among the products of the decomposition of the salts of roseocobalt and purpureocobalt. This is especially remarkable, because the constitution of roseocobalt is simpler than that of luteocobalt, the former base being $5NH^3 . Co^2O^3$, while the latter is $6NH^3 . Co^2O^3$. We have here a singular inversion of the usual law, that the products of the decomposition of a complex molecule are more simple in constitution than the body decomposed.

Luteocobalt, like roseocobalt, is a triacid base.

Chloride of Luteocobalt.—When an ammoniacal solution of chloride of cobalt, to which a large quantity of coarsely powdered chloride of ammonium has been added, is exposed to the air for some days, it often happens that no traces of chloride of roseocobalt or purpureocobalt are found, but the bottom of the vessel becomes covered with orange-yellow crystals, which are the chloride of luteocobalt. Hydrochloric acid precipitates an additional quantity of the salt from the supernatant liquid. The raw chloride, as thus obtained, is easily purified by solution in hot water, filtration, and repeated crystallization. This method of preparing the salt is by no means always successful, and very frequently results only in the formation of chloride of roseocobalt and purpureocobalt, with scarcely a trace of the chloride of luteocobalt. We have, however, almost invariably succeeded in preparing, by this process, a mixture of the sulphate and chloride of luteocobalt, by employing a solution containing both the chloride and sulphate of cobalt. The sulphato-chloride resulting, by boiling with hydrochloric acid and chloride of barium, yields a solution from which the pure chloride may be obtained by repeated crystallization. The chloride of luteocobalt crystallizes by slow evaporation, in remarkably beautiful brownish-orange coloured crystals, which belong to the trimetric or right rhombic system, and which are isomorphous with the sulphate of luteocobalt.

Fremy states that this salt crystallizes in regular octahedrons; in this case it must be dimorphous, but we have never observed any forms belonging to the regular system.

The chloride of luteocobalt is readily soluble in boiling water, and crystallizes in a great measure from the solution on cooling. Hydrochloric acid and alkaline chlorides precipitate it unchanged. When boiled with sulphuric acid, the salt gives off abundance of hydrochloric acid gas, but it is difficult to drive off all the acid without decomposing a portion of the resulting sulphate. The salt is slowly decomposed by boiling ammonia, chloride of ammonium, and a dark-brown oxide of cobalt being the only products of the decomposition which we have been able to detect. Reducing agents in general act upon this salt as upon chloride of roseocobalt and purpureocobalt. We have not yet, however, been able to obtain with the chloride of luteocobalt compounds analogous to those which are produced by the action of sulphurous acid and deutoxide of

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nitrogen upon the chlorides of roseocobalt and purpureocobalt, although we have repeatedly made the attempt.

The chloride of luteocobalt is dichrous. In the dichroscopic lens the ordinary image is pale violet, while the extraordinary image is orange-violet. The colour of the salt, in coarse powder, approaches the orange-yellow of the first circle, but the colour of the mass of crystals could not be defined by the chromatic scale, which we employed. Chloride of luteocobalt exhibits a remarkable tendency to form chloro-salts with metallic chlorides. These salts are formed with great ease, by the direct union of the two chlorides, and are worthy of notice for their stability and capacity of crystallization. Of these salts, which are very numerous, we have examined only the compounds with gold and platinum.

The analyses of chloride of luteocobalt lead to the formula

$$6NH^3 . Co^2 Cl^3,$$

	Equivs.		Theory.	Mean.	Found.			
Cobalt ..	2	59·0	22·06	22·05	22·05	22·01	22·11	22·02
Chlorine	3	106·5	39·79	39·73	39·68	39·78		
Hydrogen	18	18·0	67·3	6·70	6·68	6·73		
Nitrogen	6	84·0	31·42	31·41	31·49	31·34		

The formula $6NH^3 . Co^2 Cl^3$ is given by both Fremy and Rogojski, and no reasonable doubt can be entertained of its accuracy. The density of the chloride of luteocobalt, as taken in alcohol, is 1·7016 at 20° C., its atomic volume is consequently 157·2.

The reactions of the chloride of luteocobalt are as follows:—Iodide of potassium gives a bright yellow precipitate. Bromide of potassium gives a less brilliant yellow precipitate. Ferrocyanide of potassium gives a chamois-coloured precipitate, which becomes black on boiling. Ferridcyanide of potassium gives beautiful yellow needles, which are nearly insoluble. Cobalticyanide of potassium gives a pale fawn-coloured precipitate of fine needles. Terchloride of gold gives bright yellow granular crystals of the chloroaurate. Bichloride of platinum gives yellow or orange-yellow needles of the chloroplatinate. Chromate of potash gives a bright yellow precipitate of the chromate. Oxalate of ammonia gives a buff yellow precipitate, soluble in oxalic acid. Tribasic phosphate of soda gives, after a short time, a yellow precipitate. Pyrophosphate of soda gives a pale buff-coloured precipitate. Picrate of ammonia gives a beautiful yellow precipitate of very fine silky needles. Alkalies and their carbonates produce no precipitate in the cold. Sulphide of ammonium gives a black precipitate.

Chloroplatinate of Luteocobalt.—Chloride of platinum produces, immediately, in a solution of the chloride of luteocobalt, a beautiful orange or yellow precipitate of the chloroplatinate. When the solutions employed are concentrated, the precipitate is orange-coloured; when the solutions are dilute, yellow needles are thrown down. The difference is here only in the quantity of water of crystallization, and the orange granular crystals may be converted into the pale yellow

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needles by solution in a large quantity of hot water and recrystallization.

According to Prof. Dana's measurements, the acicular crystals belong to the monoclinic system, so far as it is possible to determine. The crystals are usually hollow and much striated longitudinally.

The salt is very slightly soluble in cold water, but dissolves in much boiling water, from which it separates on cooling. When gently heated in a porcelain crucible it gives off ammonia and chloride of ammonium, and becomes green. The green mass, on solution in water, gives globular aggregations of minute crystals of a buff colour, which may be a new salt, but which we have not specially examined. Zinc decomposes the chloroplatinate of luteocobalt only by very long boiling in an acid solution, metallic platinum being separated as a black powder, while chlorides of cobalt and ammonium are formed.

The formula of the orange salt is

$$6NH^3 . Co^2 Cl^3 + 3PtCl^2 + 6HO,$$

as the following analysis shows:—

	Equivs.	Calculated.	Found.
Cobalt.....	2	7·10	7·05
Platinum.....	2	35·64	35·41

The formula of the yellow salt is

$$6NH^3 . Co^2 Cl^3 + 3PtCl^2 + 21HO,$$

as appears from the analysis:—

	Equivs.	Calculated.	Found.
Platinum.....	3	30·99	31·16
Chlorine.....	9	33·42	33·54

Rogojski found in this salt but one and a half equivalent of water, but his analyses are not very satisfactory, giving a large excess of platinum, hydrogen, and cobalt.

Chloroaurate of Luteocobalt.—A solution of terchloride of gold produces immediately in solutions of the chloride of luteocobalt a beautiful yellow precipitate of small granular crystals. These crystals are very insoluble in cold water, but more readily soluble in boiling water acidulated with hydrochloric acid. Reducing agents separate gold with full metallic lustre. The formula of this salt is

$$6NH^3 . Co^2 Cl^3 + AuCl^3,$$

as the analyses satisfactorily show:—

	Equivs.	Calculated.	Found.
Cobalt.....	2	10·33	10·53
Gold	1	34·50	34·62
Chlorine.....	6	37·30	37·36

Iodide of Luteocobalt.—Iodide of potassium produces immediately solutions of the chloride, sulphate, or nitrate of luteocobalt, a remarkably beautiful bright yellow precipitate of the iodide of luteo-

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cobalt. This precipitate is rather insoluble in cold water, but readily soluble in hot water. The solution yields by spontaneous evaporation brown-yellow crystals, which appear to have the same form as the chloride. 0·2224 gr. of this salt gave 0·06308 gr. sulphate of cobalt, corresponding to 10·79 per cent. cobalt. The formula $6NH^3 . Co^2 I^3$ requires 10·88 per cent. cobalt.

The colour of the precipitated and dried iodide is very fine, and its brilliancy led us to hope that it might be advantageously employed as a pigment. On trial, however, the colour was found wanting in body; the yellow, moreover, changes to a brown-yellow when the powder is ground in oil or water.

Bromide of Luteocobalt.—Bromide of potassium gives a rather dull yellow precipitate in solutions of luteocobalt. The precipitate, re-dissolved in hot water, gives, on slow evaporation, wine-yellow crystals of the bromide. These crystals have the same form as those of the chloride, and their formula is therefore $6NH^3 . Co^2 Br^3$.

Cobalticyanide of Luteocobalt.—Cobalticyanide of potassium produces in solutions of luteocobalt a pale yellowish flesh-coloured precipitate of the double cyanide of cobalt and luteocobalt. The salt is insoluble in cold water, and easily decomposed by boiling water. It cannot therefore be re-crystallized for analysis. Under the microscope the crystals are seen to belong to the oblique rhombic system; they are too small to admit of accurate measurement. The formula of this salt is $6MH^3 . Co^2 Cy^3 + Co^2 Cy^3 + HO$.

	Equivs.	Calculated.	Found.
Cobalt	4	30·57	30·88
Carbon	12	18·70	18·82
Hydrogen	19	4·93	5·19

A solution of ferridcyanide of potassium produces a most beautiful precipitate of orange-yellow needles in solutions of luteocobalt. These, under the microscope, have the same form as the corresponding cobalt salt, and their formula is therefore

$$6NH^3 . Co^2 Cy^3 + Fe^2 Cy^3 + HO.$$

Sulphate of Luteocobalt.—The sulphate of luteocobalt is easily procured mixed with the chloride, when solutions of both chloride and sulphate of cobalt are rendered ammoniacal and exposed to the air after the addition of coarsely powdered chloride of ammonium in large excess. The mass of yellow crystals formed upon the bottom of the vessel, after a few days, is a mixture of the two salts. To obtain the sulphate from this mass, the solution in hot water is to be filtered and digested with sulphate of silver, after addition of a few drops of sulphuric acid. In this manner the whole of the chloride may be decomposed, and the filtered solution on evaporation will yield fine crystals of the sulphate. We have frequently prepared large quantities of the sulphate by this method. Another mode of preparing the sulphate of luteocobalt, which is often very convenient, consists in pouring ammonia upon the sulphate of roseocobalt, thrown down by cautious addition of sulphuric acid to perfectly oxidized solutions of the ammoniacal sulphate of cobalt.

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When this sulphate is powdered, and strong ammonia poured upon it, its colour frequently changes from red to a dull buff, while the supernatant liquid takes a fine red colour. The buff powder, on solution in hot water and evaporation, yields crystals of sulphate of luteocobalt. The red liquid is merely solution of sulphate of roseocobalt in ammonia. The reaction which takes place in this case may be represented by the equation—

$$5NH^3 . C^2 O^3, 3SO^3 + NH^3 = 6NH^3 . Co^2 O^3, 3SO^3,$$

the sulphate of roseocobalt simply absorbing one equivalent of ammonia. The quantity of sulphate of roseocobalt dissolved in the ammonia is very variable, being sometimes extremely small. In other cases, however, no sulphate of luteocobalt is formed, but only a solution of sulphate of roseocobalt in ammonia, from which, by evaporation, the sulphate crystallizes unchanged in large dark-red crystals. We are unable to assign a satisfactory reason for the capriciousness of the behaviour of the red sulphate towards ammonia.

Fremy asserts that sulphuric acid, cautiously added to a completely oxidized ammoniacal solution of sulphate of cobalt, throws down an acid sulphate of roseocobalt, to which he assigns the formula $5NH^3 . Co^2 O^3, 5SO^3 + 5HO$. When this acid sulphate is boiled for a few minutes with ammonia, a yellow precipitate of sulphate of luteocobalt is thrown down. The author does not attempt to explain the reaction which takes place in this case, but states that the red mother-liquor from which the sulphate of luteocobalt has separated, yields on evaporation crystals of the neutral sulphate of roseocobalt. We have never succeeded in preparing an acid sulphate of roseocobalt by the process above mentioned, nor by any other. On the contrary, we have uniformly found that sulphuric acid precipitates from the oxidized solution only the neutral sulphate of roseocobalt in small bright-red crystals, easily recognized by their form. Fremy's salt must have contained free sulphuric acid, in consequence of imperfect washing.

When a pure solution of the sulphate of roseocobalt is boiled, ammonia is evolved, while sulphate of ammonia and sulphate of luteo cobalt remain in solution, and a dark-coloured oxide of cobalt is precipitated. From the solution the sulphate of luteocobalt may be obtained by evaporation and crystallization. This method yields but little, and is not to be recommended.

Sulphate of luteocobalt is also sometimes obtained, with other products, by digesting sulphate of roseocobalt with sulphuric acid, before the period of complete decomposition sets in.

A very simple and easy method of preparing the sulphate of luteocobalt, consists in decomposing the dry sulphate of roseocobalt by heat. When the latter salt is gently heated in a porcelain crucible over a spirit-lamp, or better still, in a glass flask in a bath of rosin oil to about the temperature of melting lead, ammonia is given off in abundance, and the mass, which should be constantly stirred, assumes a fine purple-lilac hue. The heat, when the lamp alone is used, must never rise to low redness, and no vapours of sulphate

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of ammonia should be given off. The resulting mass is then to be dissolved in hot water, which gives a fine purple-red solution, and hydrochloric acid added in excess. An orange precipitate of sulphato-chloride of luteocobalt is immediately thrown down, which is easily purified, as above, by sulphate of silver and recrystallization. The acid mother-liquor sometimes deposits more sulphate on cooling. The supernatant liquid contains chloride of luteocobalt, chloride of purpureocobalt, and a leek-green crystalline body, which we have called provisionally *praseocobalt*, but which we have not yet carefully studied.

The sulphate of luteocobalt, like the chloride, has a fine wine-yellow colour, and crystallizes readily. The crystals belong to the right rhombic or trimetric system; they are hemihedral and isomorphous with the chloride of luteocobalt.

The sulphate is rather insoluble in cold but is freely soluble in hot water; the dilute solution is yellow, the concentrated solution dark sherry-wine-coloured. By double decomposition with salts of barium, it yields the other salts of luteocobalt. The sulphate, like the chloride, is dichrous, the ordinary image being pale rose-red, while the extraordinary image is bright orange. The colour of the salt in coarse powder approaches the orange No. 5 of the first circle.

Sulphuric acid does not precipitate this salt from its solution, but hydrochloric and nitric acids throw down in the cold mixtures of the chloride with the sulphate and nitrate. The salt is decomposed with very great difficulty by long boiling, even after the addition of a little ammonia. No new base is formed during the decomposition. When, however, the dry salt is gently heated in a porcelain crucible, ammonia is evolved; and if the heat be regulated so that no sulphate of ammonia is given off, while the mass is constantly stirred, there remains after a few minutes a red mass, which on solution in water gives a fine red liquid containing a sulphate of a red base, which is probably purpureocobalt. The reaction is, however, a very uncertain one, and has succeeded in our hands but once. We have in most cases obtained by the process described only a mixture of sulphate of luteocobalt, sulphate of cobalt, and sulphate of ammonia. We shall consider this subject more fully hereafter. Sulphuric acid, if not too dilute, readily decomposes the sulphate of luteocobalt when the solution is heated. It appears probable that there exists an acid sulphate of this base, as there is an acid carbonate, but we have not been able to obtain it as yet.

Sulphate of luteocobalt has the formula $6NH^3 . Co^2O^3, 3SO^3 + 5HO$, as the following analyses satisfactorily show. The salt analysed was dried by pressure between folds of bibulous paper only.

	Equivs.		Calculated.	Mean.	Found.		
Cobalt.....	2	59·0	16·85	16·83	16·80	16·85	16·83
Sulphuric acid	3	120·0	34·28	34·42	34·52	34·32	
Hydrogen ..	23	23·0	6·57	6·69	6·71	6·67	
Nitrogen....	6	84·0	24·00	23·97	24·00	23·85	
Oxygen	8	64·0	18·28	18·09	——	——	

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According to Fremy, the sulphate contains but four equivalents of water of crystallization. *In vacuo* or in dry air the sulphate of luteocobalt effloresces, becomes opake and reddish buff-coloured, and loses 4 equivs. or 10·13 per cent. of water.

Rogojski did not succeed in obtaining the sulphate of luteocobalt by decomposing the chloride with sulphate of silver. According to this chemist, there is produced under these circumstances a sulphato-chloride which has the formula

$$6NH^3 . Co^2 O^3, 3SO^3 + 6NH^3 . Co^2 Cl^3.$$

We have already mentioned, however, that the chloride and sulphate of luteocobalt are isomorphous, and we have accordingly found, as might be expected, that these two salts are capable of crystallizing together in all proportions, and cannot be separated by crystallization alone. To show the variation in the constitution of the mixed chloride and sulphate, it will be sufficient to give a few cobalt determinations made with the salt as prepared at different times.

0·1510 grs.	gave 0·0673 grs.	sulphate of cobalt =	16·96	per cent.	cobalt.
0·7075 grs.	„ 0·3210 grs.	„ „	17·26	„	„
0·1205 grs.	„ 0·0680 grs.	„ „	21·47	„	„

The parallel which Rogojski draws between the salt which he analysed and the sulphate of Gros's base, which Gerhardt considers as a sulphato-chloride of diplatinamin, must therefore be considered as illusory.

Chromate of Luteocobalt.—A solution of the neutral chromate of potash gives a fine yellow precipitate in solutions of the chloride, nitrate, and sulphate of luteocobalt. The precipitate is soluble in hot water, and crystallizes readily from the solution in brown-yellow crystals, which resemble those of the sulphate. We have not analysed this salt, but it is almost certain that its true formula is

$$6NH^3 . Co^2 O^3, 3CrO^3 + 5HO,$$

since it forms with chloride of luteocobalt crystallizable mixtures in various proportions, which exhibit in the greatest beauty and distinctness the characteristic forms of the crystals of the sulphato-chlorides above alluded to. The pure chromate can only be obtained by precipitating the nitrate of luteocobalt by chromate of potash, as the precipitate from the chloride always contains chlorine, and that from the sulphate, sulphuric acid.

Nitrate of Luteocobalt.—This beautiful salt is almost invariably obtained during the oxidation of an ammoniacal solution of nitrate of cobalt, and is deposited upon the bottom of the vessel in bright orange crystalline scales. The supernatant liquid is usually red, and contains nitrate of roseocobalt. The orange-yellow salt is easily purified by re-crystallization. The salt may also be easily prepared from the chloride or sulphate by double decomposition with nitrate of silver or of baryta. The nitrate of luteocobalt crystallizes readily in forms which belong to the square prismatic or dimetric system.

The crystals are usually small and often very brilliant. The salt is readily soluble in hot water, and separates in small crystals on

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cooling. Hydrochloric acid throws it down from its solution as a yellow crystalline powder; nitric acid also precipitates it, but sulphuric acid converts it into sulphate with more or less complete decomposition. The nitrate of luteocobalt is anhydrous, and has the formula $6NH^3 . Co^2 O^3, 3NO^5$, as the following analyses show:—

	Equivs.	Calcuiated.	Mean.	Found.	
Cobalt.....	2	17·00	16·93	16·98	16·89
Hydrogen ..	18	5·18	5·27	5·27	5·28
Nitrogen....	9	36·31	37·28	36·23	36·33

Fremy and Rogojski deduce the same formula from very imperfect analyses. Heat decomposes the dry nitrate of luteocobalt with a slight explosion, a black powder of an oxide of cobalt remaining. It may be remarked that the oxygen and hydrogen in this salt are exactly in the ratio to form water.

Oxalate of Luteocobalt.—When a solution of oxalate of ammonia is added to one of a soluble salt of luteocobalt, a buff-coloured precipitate of fine needles is thrown down, which is insoluble both in hot and cold water, but which readily dissolves in a solution of oxalic acid. From this solution the neutral oxalate crystallizes in beautiful prismatic crystals, having the colour of the sulphate and chloride. In dry air the crystals lose water like those of the other hydrated salts of luteocobalt. The oxalate has the formula $6NH^3 . Co^2 O^3, 3C^2 O^3 + 4HO$, which requires—

	Equivs.	Calculated.	Found.		
Cobalt	2	17·93	17·99	18·00	18·01
Oxalic acid ..	3	32·82	32·95	——	——

It would *à priori* appear probable that there exists an acid oxalate of luteocobalt corresponding to the acid carbonate, but we have not yet been able to obtain such a salt. The oxalic acid in this compound cannot be easily reduced by a solution of terchloride of gold, nor can it be completely separated from the base by means of a solution of chloride of calcium.

Carbonates of Luteocobalt.—The neutral carbonate of luteocobalt is readily formed by decomposing a solution of chloride of luteocobalt by carbonate of silver. The yellow solution, by evaporation, yields sherry-wine coloured crystals of the carbonate. The salt closely resembles the other soluble salts of luteocobalt, is easily soluble in hot water, and crystallizes well by slow evaporation. During evaporation, however, the solution absorbs carbonic acid from the air, and crystals of the acid carbonate are found mixed with those of the neutral salt. According to Prof. Dana's measurement, the crystals of the neutral carbonate belong to the trimetric system, and approach arragonite in form.

The constitution of the neutral carbonate appears to be represented by the formula $6NH^3 . Co^2 O^3, 3CO^2 + 7HO$, which requires—

	Equivs.	Calculated.	Found.
Cobalt	2	18·79	18·61
Carbonic acid	3	21·01	22·34

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The excess of carbonic acid and the deficiency in cobalt, are doubtless due to the presence of a portion of the acid carbonate. The neutral carbonate loses its water of crystallization in dry air, and becomes opake, with the lustre of porcelain, like many other hydrated salts of this base.

The acid carbonate of luteocobalt is most readily prepared by passing a current of carbonic acid gas into a solution of the neutral salt. The acid carbonate usually separates, after a very short time, in the form of large brown-red or sherry-wine coloured crystals, which are less soluble than those of the neutral carbonate. According to Prof. Dana, the crystals of this salt belong to the monoclinic system, and closely approach barytocalcite in form.

The acid carbonate of luteocobalt retains its water of crystallization in the air, but loses it under the air-pump. The salt is particularly interesting as being the only acid salt of luteocobalt which we have as yet been able to obtain. The formula of this salt is $6NH^3 . Co^2 O^3, 3CO^2 + HO, CO^2 + 5HO$, which requires—

	Equivs.	Calculated.	Found.
Cobalt	2	18·04	18·12
Carbonic acid	4	26·91	26·93

The very distinctly marked triacid character of luteocobalt, considered as a base, renders it, to say the least, improbable that the formula of this salt should be written $6NH^3 . Co^2 O^2 . 4CO^2 + 6HO$.

Oxide of Luteocobalt.—The oxide of luteocobalt may be obtained by decomposing a solution of the sulphate with baryta water. The solution is brown-yellow, and has an alkaline taste and reaction. It cannot be evaporated without decomposition, ammonia being evolved and a black powder separated. The solution absorbs carbonic acid from the air, and on evaporation, yields crystals of the carbonates; with acids it yields the salts of the base. The oxide of luteocobalt appears to form compounds with salts of copper, which may be analogous to the ammonia-salts of that metal, or which again may be only double salts of copper and luteocobalt. A solution of the oxide added to one of sulphate of copper gives, after standing, beautiful chrome-green crystals of a new salt, which we have not yet had an opportunity of examining.

[To be continued.]

On the Preparation of a beautiful crimson Antimonial Cinnabar. *By* Professor Böttger.

Into a porcelain dish is put 1 part by weight of officinal chloride of antimony (spec. grav. 1·35), and to it is added a solution of hyposulphite of soda, consisting of 1½ part by weight of the salt and 3 parts of water. It is then slowly heated, and constantly stirred until nothing more will separate from the fluids. In this way a compound of sulphur and antimony of a beautiful crimson colour is obtained; but care must be taken that before washing it upon the filter the adherent mother-liquor may drain away as much as possible, and that the cinnabar is not then brought in contact

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with water, as the chloride of antimony still existing in the mother-liquor might readily cause a contamination of the cinnabar, in consequence of the formation of powder of algaroth. The preparation is therefore washed first of all with very dilute acetic acid, and finally with water.

If antimonial cinnabar be boiled with a solution of carbonate of soda, it becomes converted into mineral kermes. By treatment with acetic acid, oxalic acid, phosphoric acid formic acid boracic acid, citric acid, tartaric acid, and sulphuric acid, diluted with eight times its quantity of water, or with a solution of binoxalate of potash or hyposulphite of soda, it is not decomposed either when cold or hot; it even appears to gain in intensity of colour by treatment with the above-mentioned substances. On the other hand, it is readily decomposed by muriatic acid, and by nitric acid of spec. grav. 1·2, and also, when heated, by chromic acid. Caustic ammonia dissolves it imperfectly; but it is completely and easily dissolved with the assistance of heat by solutions of soda and potash, forming a fluid which may be employed with advantage in certain cases for the blackening of objects of polished copper.—*Polytechn. Notizblatt.* 1857. No. 6.

On Copulations of Benzoin with Acid Groups. By N. Zinin.

The chlorides of the acid radicals readily act upon benzoin; hydrochloric acid is formed, and a body is obtained which is formed from benzoin by the substitution of acid groups for hydrogen. If the acid group be indicated by x, we have

$$C^{28}\,H^{12}\,O^4 + x\,Cl = C^{28}\,H^{11}\,(x)\,O^4 + HCl.$$

In this way

Chloride of acetyle furnishes acetylbenzoin.
Chloride of benzoyle furnishes benzoylbenzoin.

Benzoylbenzoin, $C^{42}\,H^{16}\,O^6$, is insoluble in water, sparingly soluble in alcohol, and soluble in 6 parts of boiling alcohol of spec. grav. 0·863. From this solution it crystallizes in the form of thin, colourless needles, resembling benzoin. By the spontaneous evaporation of the solution in æther, in which it dissolves readily, it is obtained in shining rhombic prisms. At 257° F. it fuses. It is easily soluble in chloride of benzoyle. Aqueous solution of potash does not act upon it; towards an alcoholic solution of potash it behaves like benzoin. Muriatic and sulphuric acids have no action upon it. Chlorine does not act upon it, even when fused. By treatment with nitric acid, the

Nitro-compound, $C^{42}\,(H^{15}\,NO^4)\,O^6$, may be obtained from it in crystals which fuse at about 279° F.

Acetylbenzoin, $C^{32}\,H^{14}\,O^6$, is not attacked by solution of potash, muriatic acid, or sulphuric acid. With alcoholic solution of potash it furnishes acetate and benzoate of potash. Strong nitric acid furnishes two nitro-compounds, in the form of a turpentine-like,

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thickly-fluid mass, which is insoluble in water, but readily soluble in alcohol, and still more so in æther.—*Bull. St. Pétersb.* xv. p. 282.

On the Preparation of Potassium and Sodium.
By Prof. J. R. WAGNER.

The high price of aluminium and the rarity of magnesium, calcium, strontium, barium, and other metals are caused, as is well known, entirely by the great cost of the sodium or potassium necessary to separate them from their compounds. A proposition made by the author five years ago, to employ an alloy of sodium and potassium for purposes in which the metals are only destined to act as reducing agents, appears to have remained unnoticed, although a favourable result might be expected from it.

This proposition is founded upon the circumstance, that as the fusing-point of an alloy of potassium and sodium is far lower than that of either of the two metals by itself, the boiling-point and the temperature required for the reduction of the alloy of potassium and sodium will also be lower than those of either of the constituents. It might therefore be attempted to prepare an alloy of potassium and sodium directly, by heating a mixture of carbonates of soda and potash, chalk and charcoal powder, in accordance with Deville's process, and employ this in the preparation of aluminium, &c.

Dumas, however, recommended twenty-five years ago, in order to facilitate the reduction of the salt of soda in the preparation of sodium, that the carbonate of soda or caustic soda to be decomposed, should be mixed with a little potash, and the alloy of sodium and potassium produced separated by slow oxidation.—Dingler's *Polyt. Journal*, cxliii. p. 343.

PROCEEDINGS OF SOCIETIES.

Royal Society.

March 12, 1857. (Major-General Sabine, Treas. and V.P., in the Chair.)

"On the Immediate Principles of Human Excrements in the Healthy State." By W. Marcet, M.D., F.C.S.

In a previous paper* I had the honour of communicating to the Royal Society the results of a first series of investigations on the immediate principles of the fæces of man and animals; since then I have continued my researches on human excrements, being most ably seconded by my assistant, Mr. Frederick Dupré, Ph.D.

The new results obtained were the following:—

1. *Margarate of lime, phosphate of lime,* and *margarate of magnesia* were discovered to be immediate principles of human evacuations.

2. I found a new method for obtaining excretine, and its chemical formula has been established.

3. The fact that vegetable food induces the presence of margaric acid in excrements has been confirmed.

* See Chem. Gaz. vol. xii. p. 378.

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4. The existence of a comparatively large quantity of cholesterine in the spleen, which I had mentioned before as probable, has been confirmed.

When human fæces are exhausted with boiling alcohol, the fluid being rapidly strained through a cloth, a clear extract is obtained, which, on cooling, yields a deposit; this substance, being collected on a filter, is partly soluble in boiling alcohol, and there remains undissolved a residue insoluble in ether and alcohol. The residue in question being boiled with a solution of potash, dissolves almost entirely, and the addition of hydrochloric acid induces the formation of a precipitate in the solution. On examining this precipitate, it was found to consist of a crystallizable substance fusing at 60° Cent.; its structure and other properties were precisely those of *margaric acid*.

The acid filtrate contained *phosphoric acid* and *lime*. From several quantitative analyses, I concluded that there was more lime than is required to combine with the phosphoric acid in the form of the neutral phosphate, the excess of lime being exactly that which was necessary to convert the margaric acid into a neutral margarate of lime, $C_{34}H_{33}O_3+CaO$. Consequently it followed that the three substances existed in the form of *margarate of lime* and *phosphate of lime* as immediate principles of human fæces.

The alcoholic filtrate from the deposit being allowed to stand for twenty-four hours, deposited another substance, of a nearly white appearance, and which proved to be *margarate of magnesia*.

The peculiar action of a vegetable diet on human fæces was investigated by means of experiments undertaken upon myself, when I observed that an entirely vegetable diet was attended with the formation of a large quantity of margaric acid in the excrements,—most probably not in the form of a margarate, but in the free state, inasmuch as it was obtained from the decomposition, with hydrochloric acid, of the precipitate induced by adding milk of lime to the cold and clear alcoholic extract of fæces, after the separation of the above-described deposits.

In the month of December 1855, I had an opportunity of noticing that during a cold night, when the temperature falls below the freezing-point, *excretine* crystallizes readily and in large quantity in the clear alcoholic extract of fæces; this method I employed as often as possible, to prepare enough excretine for its chemical analysis; but the cold weather not lasting long enough, and this season having been remarkably mild, I was compelled to adopt a modification of the process by milk of lime, described in my former communication.

Having prepared a sufficient quantity of excretine, partly by the action of cold, and partly by means of milk of lime, the chemical composition of this substance was now determined. A qualitative analysis showed it to consist of carbon, hydrogen, sulphur and oxygen*; there was no water of crystallization present. Oxide of

* In my former communication I had erroneously stated that excretine contained nitrogen, which resulted from my not having been able to prepare a sufficiently large quantity of the substance; and, moreover, it might not have been perfectly pure.

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copper was employed at first for the combustions, but they were subsequently undertaken with chromate of lead, on account of the large proportion of carbon that excretine contains; no substance having been found to combine with it, its atomic composition was calculated from the assumption that one equivalent contained one equivalent of sulphur; and the following formula was obtained:—

78 eq. Carbon	468
78 eq. Hydrogen	78
1 eq. Sulphur	16
2 eq. Oxygen	16
Atomic weight of Excretine	578

In my former communication I had stated that when the tissue of the spleen is submitted to a process of analysis similar to that adopted for the extraction of excretine, a substance closely allied to cholesterine is obtained. This subject being one of great importance in a physiological point of view, I have resumed the investigation, and placed beyond doubt that this substance is really *cholesterine*. Its presence in the spleen is evidently independent of that which might exist in the blood retained by this organ after death. Is it that the spleen secretes cholesterine? This can only be determined by actual experiment; but it is very remarkable that a part of the blood which is supplied to the liver should come directly from an organ containing large quantities of a substance known to enter into the composition of the bile.

April 2, 1857. (The Lord Wrottesley, President, in the Chair).

"Researches on Silica." By Colonel Philip Yorke, F.R.S.

This communication is principally devoted to an attempt to determine the formula of silica, and to the relation of some remarkable results obtained in this research. After giving some account of the grounds on which the three different formulas now in use among chemists (viz. SiO_3, SiO_2, and SiO) had been advocated, the author proceeds to state, that it appeared to him that the direct method which had been followed by Rose deserved the preference. This method consists in determining the quantity of carbonic acid which is displaced from excess of an alkaline carbonate in fusion, by a given weight of silica. The number 22 being the equivalent for carbonic acid on the hydrogen scale, the equivalent of silicic acid is obtained by the proportion $x = \frac{22 \times \text{weight of silica used}}{\text{weight of carbonic acid expelled}}$.

Four experiments are detailed, made with carbonate of potash, which give as a mean result the number 30·7 for the equivalent of silica. This agrees with the formula SiO_2, and nearly with the previous results of H. Rose. Then follow seven experiments made in a like manner with carbonate of soda, which give as a mean result the number 21·3 as the equivalent of silicic acid—a number agreeing nearly with half that represented by the formula SiO_3, or $\frac{45 \cdot 2}{2}$.

Some experiments are then related, which go to show that the increased loss resulting with carbonate of soda could not be caused

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by the action of heat alone.—The author had next recourse to carbonate of lithia, and obtained as the mean result of four experiments with this substance, agreeing well together, the number 14·99 —a number which accords very closely with the formula SiO. These different numbers, obtained with silica, led the author to inquire whether any other body acting as an acid produces similar results with the fused carbonates of potash and soda. With this view, experiments were made with dry sulphate of magnesia, as a substitute for sulphuric acid, with bi-borate of soda, for boracic acid, with alumina and sesquioxide of iron. Of these bodies only boracic acid gave results similar to those obtained with silicic acid. The other substances all gave the equivalent numbers usually assigned to them, equally with the carbonates of potash and soda.

Directing his attention then to determine whether the equivalent of silicic acid could be found in other volatile acids than the carbonic, the author relates some experiments made with the hydrates of potash and soda, but he explains that there are circumstances which render it much more difficult to obtain accordant numbers with these bodies than with the carbonates.

Six experiments made with hydrate of potash gave as mean result the same number as that obtained with the carbonate, viz. 30·8. But with hydrate of soda the mean of three experiments gave the number 17·2 as the equivalent of silicic acid,—a result approaching that previously obtained with carbonate of lithia.

A silicate of soda was formed by fusing together silica and carbonate of soda, in proportions indicated by the previous experiments—*i. e.* 23 silica to 54 carbonate of soda = 31 soda. The fused mass was crystallized. It was dissolved in water, and the solution evaporated *in vacuo* yielded a crystallized salt, which contained about 5 per cent. of carbonate of soda; when this, calculated as the ordinary 10-hydrated salt, was subtracted, the silicate agreed nearly with the formula $NaO.SiO_2+7HO$. A crystallized salt of like composition was obtained when hydrated silica was dissolved in a solution of caustic soda, the silica and soda being in the same proportions, *i. e.* 31 : 23. In these experiments it appears, therefore, that in the process of solution and crystallization a portion of soda is extruded. When exposed to a temperature of about 300° F., nearly all the water was driven off from these salts, less than 1 per cent. remaining.

The fused silicate of lithia in like manner, when treated with water, appeared to split up into different compounds.

After guarding himself from drawing any decided inference from the experiments recorded, the author concludes by observing that at present he can see no alternative but to admit of more than one equivalent for silicic acid (that is to say of more than one acid), the value of which is determined by circumstances,—such as the presence of water and the nature of the base to which it is presented. The existence of such different silicic acids has been already suggested by chemists on different grounds, particularly by Ebelman and Laurent, and lately by M. Fremy.

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THE CHEMICAL GAZETTE.

No. CCCLV.—August 1, 1857.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Boron; its Analysis and Physical Properties.

By F. Wöhler *and* H. Sainte-Claire Deville.

Since the authors' previous paper* on boron, they have prepared a great many specimens of crystallized boron, and examined its physical properties with great care, analysing the substances operated upon each time. Their present paper contains the result of these experiments.

Boron, as previously stated by the authors, is obtained of very different colours, from a garnet-red so deep as almost to produce opacity to a nearly colourless honey-yellow. The analysis of the substance in these different states showed that its composition changed a little simultaneously with its colour. There are three distinct varieties which appear to possess the same crystalline form, judging from some angles which have been measured upon two of them. But one of these varieties has been obtained in crystals so distinct and reflective that the angles could be determined with precision; the crystalline form of boron is the right prism with a square base, the parameters of which, calculated from the inclinations of the faces of the most developed octahedron of the crystal, are in the proportion of 1 for the horizontal axes to 0·816 for the vertical axis. The forms found are,—two octahedra (111), (221), supported upon the edges of the base, the faces (110) of the prism, and (100) of a second prism, the faces of which are tangents to the edges of the former. The angles of these faces allow us to regard boron as perfectly isomorphous with tin. The colour of the crystal measured was deep garnet-red, but transparent.

The density of boron is 2·68, or a little more than that of silicium. The density of silicium is equal to that of silica; that of boron is distinctly superior to that of boracic acid, and the density of the diamond is very great in comparison to that of liquid carbonic acid. Aluminium, which comes before silicium, has a density which is scarcely two-thirds of that of corundum. The hardness of boron varies greatly in different specimens, but is always much superior to that of corundum. In this respect the authors distinguish three varieties of crystals.

I. Boron in laminæ of a metallic lustre at least equal to the lustre

* See Chem. Gaz., May 1, 1857, p. 161.

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of the diamond; it appears black and opake, but transparent in the thinner parts of the crystal. This boron is very cleavable, which renders the crystals rather brittle; its hardness is considerable, and it distinctly scratches the diamond. Some experiments made by M. Quillot, show that the boron acts upon the diamond more slowly than the diamond itself, and that in course of time the tool bearing the powder of boron becomes sticky, which indicates a hardness less than that of the diamond. This variety of boron is always produced when the boracic acid and aluminium are left in contact for but a short time, or when the operation is performed at a low temperature. This boron is composed of

Carbon.....	2·4
Boron	97·6

The analysis of boron is a delicate operation which presents some difficulties. The following was the process adopted:—The boron was weighed, placed in a platinum tray, and burnt in a long tube of Bohemian glass, heated at the spot where the tray was placed, that is to say close to the point at which the chlorine arrived, to such a temperature that the glass softened. Fuming chloride of boron was evolved and lost; the residue is carbon, which was weighed and burnt in oxygen gas, collecting the carbonic acid. The carbon often retains the form of the crystals of boron which were put into the tray. In this operation there is always formed a small quantity of a slightly yellowish-white sublimate, which becomes heated by contact with water, and dissolves therein almost completely in course of time. It contains chloride of sulphur, produced by the action of chlorine upon the vulcanized India-rubber, and boracic acid, the oxygen of which is furnished by the air carried along by the current of chlorine, or by the moisture of the gas. In this way a volatile, solid substance is formed, decomposable by water into muriatic and boracic acids; it is obtained in considerable quantities during the preparation of chloride of boron.

This sublimate may also contain aluminium. To detect this, the solution is evaporated almost to dryness, and a little hydrofluate of fluoride of sodium (or hydrofluate of ammonia) and an excess of sulphuric acid are added. The evaporation is continued to the point at which the sulphuric acid becomes vaporized. It is then treated again with water. The filtered solution leaves a small quantity of sandy matter arising from the silica, either of the fluoride of sodium or of the boron itself; when treated with ammonia and boiled, it did not furnish alumina.

II. Boron is also obtained in perfectly limpid and transparent crystals, grouped in the form of long prisms, so as to represent the teeth of a saw. Sometimes very small ones are obtained which are really prismatic with eight faces. Their adamantine lustre is extreme; but their hardness is a little less than that of the first variety. The prolonged action of acids, and especially of *aqua regia*, upon their surface, does not appear to be perfectly null. These crystals are obtained whenever an excess of aluminium is

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kept in contact with boracic acid for a long time in a charcoal crucible at a high temperature. It requires to be heated for at least five hours to the temperature of the fusion of nickel.

The composition of this boron is very variable. The analysis of a very fine specimen, composed of selected crystals, gave,—

Carbon	4·2
Aluminium	6·7
Boron	89·1

If rather large crystals of this substance, not macled, could be produced, they might certainly be employed in jewellery.

III. The hardest of all the varieties of boron, incomparably harder than the first, is obtained by exhausting at several times the action of a great excess of boracic acid upon aluminium, at such a temperature that all the boracic acid is very rapidly volatilized. It is for this reason that in order to obtain 1 or 2 grms. of this substance, 20 or 30 grms. of boracic acid must be volatilized in closed vessels, heating it each time for 2 or 3 hours. There then remains in the crucible a cavernous mass of a clear chocolate-red colour exactly like that variety of the diamond which is called *bowr*, beset with crystals of boron, of very great brilliancy, and from which the iron, or foreign metals, and a little aluminium must be removed by soda and muriatic acid. Unfortunately the boron cannot thus be separated from the alumina with which it is impregnated. For this reason the authors cannot give an analysis of it; but it appears to be the purest of all the varieties.

Under the microscope this mass of boron appears to be composed entirely of small crystals; very clear and distinct crystals are also perceived with the naked eye, although these are very minute. In hardness this substance does not yield to the diamond; after its employment it is found with the same degree of fineness as before, which appears to be a character of good diamond powder. It is also crushed with extreme difficulty.

With regard to the interpretation of their analysis, the authors remark that the carbon must be regarded as being in the state of diamond. The greater the quantity of carbon, the more the transparency appears to increase; and a few thousandths of black carbon suffice to give a very strong tint to glass in which it cannot be supposed that the carbon is combined with material coloured by it. It must also be admitted that the carbon has crystallized with the boron of which it does not possess the form. This hypothesis is not opposed to the facts observed in some cases in which a predominant substance is seen to impose its form upon substances with which it has a certain analogy of chemical properties. The presence of alumina in amphiboles is an example of this. Moreover, there is no reason why the diamond itself should not be dimorphic like so many other substances. The seleniuretted sulphur, obtained artificially with solutions of selenium and sulphur in sulphuret of carbon, is an example of this. By operating with certain precautions, the sulphur then takes up selenium, of course in very small

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quantities on account of the slight solubility of the latter; the presence of selenium, which has no relation of form with sulphur, may be easily proved by the analysis of the product, the measured angles of which are identical with those attributed by Mitscherlich to octahedral sulphur.

The conditions of the isomorphism of simple bodies and of their mutual attraction by crystallization, require to be studied experimentally upon the small number of these bodies which are sufficiently nearly allied in the classifications of science, that their combinations do not obey the law of equivalents, so that their contact only produces a solution. Carbon, boron, and silicium, which are so nearly allied, might mutually dissolve each other without combining, and coexist in crystallized boron, without altering its form. The contrary takes place when silver is dissolved in lead; lead crystallizes without taking with it any notable quantity of silver. It separates like an anhydrous salt from a saturated aqueous solution.

These observations apply to aluminium, the presence of which in boron in very variable proportions (from 0 to 13 per cent.) never indicates a combination; for even the formula Al,B^7 would require 20 per cent. of aluminium. This new fact may be of use in the determination of the conditions of isomorphism in simple bodies; and it may give a certain support to the opinion that aluminium should be placed in the carbon and boron group, by the same right and with the same rank as antimony in the series of nitrogen and phosphorus. —*Comptes Rendus*, February 16, 1857, p. 342.

Investigation of Pyrogallic Acid. *By* Anton Rosing.

Perfectly pure pyrogallic acid has no reaction upon litmus-paper, but the commercial acid usually has an acid reaction, due to the presence of foreign bodies. It cannot be sublimed without alteration; a part becomes decomposed and produces metagallic acid. This has prevented the determination of the density of the vapour. Dry pyrogallic acid undergoes no change under the influence of the air; on the other hand, its solution is pretty rapidly altered, acquiring a darker colour, and finally depositing a brown, amorphous substance. This decomposition must not be confounded with that which pyrogallic acid undergoes under the influence of alkalies, which the author found to take place in air washed with sulphuric acid. A few drops of muriatic acid prevent any coloration of solutions of pyrogallic acid.

Concentrated and dilute muriatic acid do not react upon pyrogallic acid, either in the cold or at a boiling heat. When monohydrated sulphuric acid is poured over dry pyrogallic acid, the crystals become yellow and gradually dissolve; if the solution be heated, it becomes black; with fuming sulphuric acid, pyrogallic acid gives a black solution. This is not a simple phænomenon of solution, for the liquid, when diluted with water, neutralized by carbonate of baryta, and filtered, gives a yellow liquid containing sulphuric acid and baryta; but as products of decomposition are formed at the

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same time, the *sulphopyrogallate* has not been obtained in a state adapted for analysis.

Fuming nitric acid reacts briskly upon pyrogallic acid. The mixture becomes heated and acquires a brown colour, evolving reddish vapours, the colour gradually becomes paler, and by evaporation crystals of oxalic acid are formed.

Chlorine gas reacts energetically upon dry pyrogallic acid, producing a black coloration and evolving muriatic acid. The author's experiments have led him to think that there is a formation of a series of chlorinated products which he has not succeeded in separating; the greatest quantity of chlorine which he has hitherto been able to introduce was about 27 per cent.

Dry iodine does not react upon the acid under ordinary circumstances, but at 392° F. in a sealed tube placed in an oil-bath, it appears to attack it.

When anhydrous bromine is poured upon dry pyrogallic acid, a brisk reaction takes place with evolution of hydrobromic acid gas; if the excess of bromine be driven off, there remains a heavy, yellowish mass, which, when heated upon platinum-foil, takes fire, burns with a flame margined with green, and leaves much carbon. Analysis gave,—

	I.	II.	Calculated.
C	20·022	19·772	20·00
H	0·860	0·845	0·80
Br	66·100		66·00
O	13·018		13·20

which corresponds with the formula $C^{12}\,\frac{H^3}{Br^3}\,O^6$.

This product is nearly insoluble in cold water; when boiled with water it is partially dissolved, and the rest is decomposed. It is soluble in alcohol and æther. The solution is brown, and possesses a very distinct acid reaction. The alcoholic solution, when evaporated spontaneously, furnishes magnificent large crystals of a light-brown colour, which appear to be oblique rhomboidal prisms; they contain 2 equivs. of water. Muriatic and sulphuric acids do not appear to act upon this brominated product, but concentrated nitric acid acts upon it strongly, and evolves reddish vapours. With ammonia a solution of the product acquires a very intense red colour, which becomes brown by the action of the air. Potash and soda produce an analogous reaction. With protosulphate of iron, the solution acquires a very rich blue colour, comparable to Saxony blue or ammoniacal oxide of copper. The sensibility of this reaction is such, that the substance might replace ferrocyanide of potassium for detecting protoxide of iron. The blue liquid remains for a long time unaltered in the air, but at length its colour becomes black, and a viscous mass is deposited, containing crystalline laminæ insoluble in cold water, but soluble in alcohol.

In the absence of air, for example in a current of hydrogen, dry ammoniacal gas has no action upon dry pyrogallic acid. When the excess of gas is driven off, there remains a quantity which may rise

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to 2 per cent., but this gas is gradually set free *in vacuo*, and the acid remains unaltered.

With an excess of ammonia in contact with the air, a solution of pyrogallic acid becomes of an extremely dark-brown colour; spontaneous evaporation leaves a black, amorphous substance, of a resinous appearance. This product possesses the following properties. It evolves ammonia when heated with slaked lime, and also, but with difficulty, with a solution of potash; it dissolves in water and alcohol with a brown colour so intense and pure that it might be employed as sepia. The solution is neutral with litmus-paper, and gives precipitates with a great many metallic salts, &c.,—such as acetate of lead, sulphate of copper, chloride of manganese, sulphate of iron, bichromate of potash, and lime-water. The lead precipitate at least is a nitrogenous product. This product is of variable composition, so that no formula can be given for it, but there is no doubt that the principal reaction consists in an oxidation with fixation of nitrogen, at the same time apparently with elimination of hydrogen.

Numerous experiments of ætherification with pyrogallic acid gave negative results. Contrary to what has been said, pyrogallic acid does not set free carbonic acid from the carbonates of lime, ammonia, &c., nor from bicarbonates; but under the influence of the air a solution of pyrogallic acid, mixed with an alkaline carbonate, slowly becomes brown.

Pyrogallic acid reduces not only the noble metals from their solutions, but also copper in the saccharimetric fluid of Frommherz, towards which it behaves like glucose; it combines with different metallic oxides, forming compounds, the powerful affinity of which for the oxygen of the air renders their preparation very difficult. It also combines with certain organic substances, such as gelatine and caseine.

A mixture of pyrogallic and stearic acids submitted for 36 hours to a temperature of 392° F. in a sealed tube, furnishes a crystallized compound, from which, however, the excess of stearic acid may be separated.

From his experiments, many of which he regards as preliminary, the author deduces as a general conclusion that pyrogallic acid is not a true acid; of all known bodies it most closely approaches orcine. It shares its rapid alterability under the influence of air and bases; it absorbs dry gaseous ammonia, but loses it afterwards *in vacuo*; with aqueous ammonia, under the influence of air, it furnishes a neutral nitrogenous compound, &c. This comparison may be followed even in its mode of production, for

$$\underbrace{C^{16}H^{8}O^{8}}_{\text{Orsellic acid.}} = C^{2}O^{4} + \underbrace{C^{14}H^{8}O^{4}}_{\text{Orcine.}},$$

$$\underbrace{C^{14}H^{6}O^{10}}_{\text{Gallic acid.}} = C^{2}O^{4} + \underbrace{C^{12}H^{6}O^{6}}_{\text{Pyrogallic acid.}}.$$

It might be advisable to replace the term *pyrogallic acid*, by *pyrogalline*, or simply *galline*. In this case the brown, nitrogenous

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product might be called *pyrogalleine* or *galleine*, by analogy with *orceine*.

At the same time pyrogallic acid presents some characters analogous to those of some pyrogenous acids, especially of pyromeconic acid, and it would not be impossible to unite these bodies in a single group. Thus we have—

$$\underbrace{C^7\ H^2\ O^7}_{\text{Meconic acid.}} = C^2\ O^4 + \underbrace{C^5\ H^2\ O^3}_{\text{Pyromeconic acid.}},$$

$$\underbrace{C^8\ H^4\ O^{10}}_{\text{Tartaric acid.}} = C^2\ O^4 + \underbrace{C^6\ H^4\ O^6}_{\text{Pyroracemic acid.}},$$

$$\underbrace{C^{14}\ H^4\ O^{14}}_{\text{2 equivs. Meconic acid.}} = C^2\ O^4 + \underbrace{C^{12}\ H^4\ O^{10}}_{\text{Comenic acid.}},$$

$$\underbrace{C^{12}\ H^6\ O^{12}}_{\text{Aconitic acid.}} = C^2\ O^4 + \underbrace{C^{10}\ H^6\ O^8}_{\text{Itaconic acid, &c.}}.$$

These four pyrogenous acids, the mode of production of which is analogous to that of pyrogallic acid, present several properties common to the latter, and amongst others that of striking a red colour with the persalts of iron.—*Comptes Rendus*, June 1, 1857, p. 1149.

On the Decomposability of the Native Silicates by Ammoniacal Salts. By M. Feichtinger.

The silicates employed for the experiments were in the state of very fine powder and were kept in contact with the aqueous solutions of the ammoniacal salts for 14 days at the ordinary temperature and frequently stirred. The fluid was then filtered off and analysed.

Stilbite (consisting of silica, alumina, and lime) and *hornblende* (consisting of silica, magnesia, protoxide of iron and alumina) were treated with a solution of nitrate of ammonia (1 part of salt to 20 parts of water). The quantity of *stilbite* employed was 0·690 grm., 0·011 grm. of lime were found in the ammoniacal solution. The quantity of *hornblende* employed was 2·860 grms. The magnesia was weighed as pyrophosphate of magnesia; the quantity was 0·008, which gave by calculation 0·0029 magnesia.

Chlorite (consisting of silica, alumina, magnesia, and protoxide of iron) and *garnets* (silica, lime, and peroxide of iron) were placed in contact with a solution of muriate of ammonia. The quantity of *chlorite* was 2·966. By analysis as pyrophosphate of magnesia, 0·014 =0·0051 of magnesia. The solution of muriate of ammonia which had been in contact with the *garnets*, showed the presence of lime distinctly with oxalate of ammonia, but its quantity was too small to enable its quantitative determination to be effected.

Analcime (silica, alumina, and soda) and *felspar* (silica, alumina, and potash) were treated with a solution of carbonate of ammonia. In both the supernatant fluid, when filtered clear, was carefully

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evaporated and heated until the ammoniacal salt was volatilized. Both left a residue which had an alkaline reaction upon reddened litmus- and turmeric-paper.

The residue from the treatment of *analcime*, when moistened with a few drops of muriatic acid and evaporated upon a watch-glass, left a slight saline residue.

The solution of the calcined residue from the treatment of *felspar*, after the addition of a few drops of muriatic acid and solution of perchloride of platinum, and after evaporation on a watch-glass and washing with dilute alcohol, left a yellow, crystalline powder, which, under the microscope, distinctly exhibited the crystalline form of platinochloride of potassium (octahedra), and the quantity of which was 5 milligrms.=1 milligrm. of potash.—Liebig's *Annalen*, June 1857, p. 353.

On Benzonitrile. *By* Hugo Schiff.

Benzonitrile, or cyanphenyle ($C^{14} H^5 N$), was first obtained by Fehling by the distillation of benzoate of ammonia. In this case benzamide seems to be formed as an intermediate step, which becomes converted into benzonitrile by loss of water, in accordance with the equations—

$$C^{14} H^5 (NH^4) O^4 - 2HO . = NH^2 . C^{14} H^5 O^2 \text{ (benzamide).}$$
$$NH^2 . C^{14} H^5 O^2 - 2HO . = C^{14} H^5 N \text{ (benzonitrile).}$$

Benzonitrile has actually been obtained subsequently by the dry distillation of benzamide; it has also been obtained by the action of perchloride of phosphorus, perchloride of benzoyle, and benzoic acid anhydride upon benzamide, these methods depending upon the separation of 2HO from the benzamide.

Limpricht and Von Uslar recently showed that the oily fluid, smelling like oil of bitter almonds, which makes its appearance in the dry distillation of hippuric acid, is nothing else than benzonitrile. By heating hippuric acid to 464° F., they prepared benzonitrile in abundance. The author describes some chemical methods by which benzonitrile is obtained.

If perchloride of benzoyle be poured over sulphocyanide of potassium, a brisk reaction takes place even at ordinary temperatures; the mixture becomes strongly heated, a strong odour of sulphuret of carbon makes its appearance, and a brownish-yellow readily triturable mass is obtained, which when distilled furnished a considerable quantity of benzonitrile mixed with sulphuret of carbon and benzoic acid. In this process it is probable that sulphocyanide of benzoyle is first formed, which, however, is again decomposed immediately, in accordance with the equations—

$$C^{14} H^5 O^2 Cl + C^2 N KaS^2 = KaCl + C^2 N (C^{12} H^5 O^2) S^2, \text{ and}$$
$$2C^2 N (C^{14} H^5 O^2) S^2 = 2C^{14} H^5 N + C^2 S^4 + C^2 O^4.$$

The brownish-yellow fluid obtained is washed with slightly alkaline water to remove the benzoic acid, then dried over chloride of calcium and rectified. The portion passing over at 374° F. contains

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much sulphuret of carbon; the distillate, which boils at a higher temperature, is still contaminated with benzoic acid. The former is extracted with dilute solution of potash, dried over chloride of calcium, and distilled with a slowly-rising temperature; the portion passing at 374° F. is again rectified by itself. In conclusion, a limpid fluid is obtained, possessing all the properties ascribed by Fehling, Limpricht and Von Uslar to benzonitrile.

Cyanate of potash was poured over with perchloride of benzoyle in a small flask, which was attached to a Liebig's refrigerating apparatus in such a way that everything that was volatilized was compelled to flow back again. After boiling for about four hours, a brown paste was produced, which on cooling solidified into a mass similar to that formed in the method just described. By dry distillation benzonitrile was obtained, but the amount was somewhat smaller than when sulphocyanide of potassium was employed. The formation of the benzonitrile is explained by the equation—

$$C^{14}\,H^{5}\,O^{2}\,.\,Cl + C^{2}\,N\,KaO^{2} = KaCl + C^{14}\,H^{5}\,N + C^{2}\,O^{4}.$$

Cyanate of potash was submitted to dry distillation with benzoic acid anhydride. With a very strong heat, a small amount of benzonitrile was obtained. The conversion probably took place in accordance with the equation—

$$C^{28}\,H^{10}\,O^{6} + 2C^{2}\,N\,KaO^{2} = 2C^{14}\,H^{5}\,N + C^{2}\,Ka^{2}\,O^{6} + C^{2}\,O^{4}.$$

Sulphocyanide of potassium was submitted to dry distillation with benzoic acid anhydride. The mixture frothed up strongly when only moderately heated, a strong odour of sulphuret of carbon made its appearance, and the author obtained a small quantity of benzonitrile, as explained by the equation—

$$C^{28}\,H^{10}\,O^{6} + 2C^{2}\,N\,KaS^{2} = 2C^{14}\,H^{5}\,N + C^{2}\,Ka^{2}\,O^{6} + C^{2}\,S^{4}.$$

The small amount in the last two experiments is probably to be ascribed to the circumstance, that a larger quantity of the benzoic acid employed was sublimed, and thus removed from the action of the decomposing cyanide. In the first two methods a greater amount may be obtained when the brown mass is repeatedly extracted with æther, and then only the last portion of benzonitrile is attempted to be recovered by dry distillation. The analysis gave—

C	79·83	81·03	..	..	14 =	84	81·55
H	5·26	5·12	5·29	..	5	5	4·86
N	..	..	..	13·44	1	14	13·59

Hofmann's statement, that no benzonitrile is obtained by the mutual action of cyanide of potassium and phenylosulphates, has been confirmed by the author. Another experiment also, to prepare sulphophenyle ($C^{24}\,H^{10}\,S^{2}$) by the dry distillation of sulphuret of potassium with phenylosulphates, gave a negative result.

Lastly, the statement that benzonitrile, when heated, is capable of dissolving a considerable quantity of sulphur, which it deposits again on cooling in flat prisms, is one which, as far as the author knows, has never yet been confirmed.—From the author's *Inaugural Dissertation*, Göttingen, 1857.

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On a new Mode of Preparation of Phosphuret of Nitrogen. *By* Dr. Pauli.

Amorphous phosphorus and sulphur may be fused together without the occurrence of an explosion; in this way therefore the sulphur compounds of phosphorus may be prepared.

If a mixture of pentasulphuret of phosphorus with muriate of ammonia be heated in a retort, muriatic acid, sulphuretted hydrogen, muriate of ammonia, and sulphuret of ammonium are evolved. When the evolution has ceased, if the retort be broken, it is found to contain a yellow powder, which is light, like magnesia. This is triturated, put into a new retort, and again heated; the retort is again broken and the powder again triturated, and this is repeated until no more muriate of ammonia is evolved on the application of heat. The author's analyses prove that this phosphuret of nitrogen contains a mixture of phosphuret of nitrogen, PN^2, with phosphamide, N^2PH. This compound, consisting of—

PN^2 77·508
and PN^2H 22·492,

has the following properties:—

It is insoluble in water and fuming nitric acid; when fused with crystallized caustic potash ($KO, 5\dot{H}O$), it evolved ammonia in abundance; and it is completely decomposed (at a red heat) by sulphuretted hydrogen gas into sulphuret of phosphorus and gaseous ammonia. When heated with metallic zinc until the latter is completely fused, a decomposition takes place with evolution of ammonia. Analysis gave,—

	Found.			Calculated.	
P	52·32	52·94	52·65	1	51·96
N	33·07	28·73	29·62	2	46·39
H	1·43	1·45	1·49	1	1·65

The formation of phosphamide, therefore, takes place in accordance with the following equation:—$3(NH^4, Cl) + PS^5 = N^2PH + 4HS + 3HCl + NH^4S$.

The same phosphuret of nitrogen is obtained,—1st, by the action of hyposulphuret of phosphorus upon muriate of ammonia; 2ndly, when pulverulent phosphuret of lime is intimately mixed with sulphur and muriate of ammonia and heated, when it is as well to mix the residue again with flowers of sulphur and muriate of ammonia even at the first change of retorts; a white insoluble powder is formed, from which nitric acid extracts phosphate of lime; it evolves ammonia with potash, and fumes of hyponitric acid with peroxide of copper.—Liebig's *Annalen*, ci. p. 41.

On the presence of Vanadium in Native Molybdate of Lead. *By* Professor Wöhler.

In some recent experiments with native molybdate of lead which I had obtained in the form of a sandy powder from Bleiberg in Carinthia, the molybdic acid was prepared therefrom according to

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the process of Elbers*. The pulverized ore was fused with carbonate of soda free from sulphuric acid and charcoal, the mass lixiviated with water, the solution supersaturated with nitric acid, and evaporated to dryness. The dry mass was reddish-yellow, and when for the purpose of separating the molybdic acid water was poured over it, a deep-yellow solution, which still contained much molybdic acid, was produced. To ascertain the cause of the yellow colour, which appeared to indicate vanadine, and remove the large quantity of nitrate of soda, the solution was boiled with sulphuret of potassium, and the metal then thrown down as sulphuret by muriatic acid. After washing and drying, it was thoroughly calcined, and the residue was dissolved in ammonia. In this solution a fragment of muriate of ammonia was placed. In proportion as this dissolved, a white powder separated, which, after being washed with solution of muriate of ammonia, proved to be vanadiate of ammonia. When heated in the air, it left dark-brown vanadic acid, which fused when more strongly heated, and on cooling solidified into a dark-red, very crystalline mass.

It now remains to discover a process by which the entire amount of vanadium may be separated more simply from the molybdenum, and also to decide whether vanadic acid is merely a fortuitous constituent of this molybdate of lead, or whether vanadiate of lead occurs as an independent mineral together with the latter.—Liebig's *Annalen*, June 1857, p. 383.

ANALYTICAL CHEMISTRY.

On some Analytical Processes applicable to Mineralogical Investigations. By M. Barreswil.

Distinctive Characters of Manganese.—When peroxide of manganese is acted upon by syrupous phosphoric acid, or by an acid phosphate, an evolution of oxygen takes place, and the peroxide disappears in the fusing mass, which acquires a magnificent violet colour, the intensity of which increases with the proportion of manganese.

If a salt of protoxide of manganese be substituted for the binoxide, the only phænomenon observed is the evolution of the acid originally combined with the protoxide of manganese, which dissolves in the limpid and colourless phosphoric acid. The violet colour may however be produced in this liquid by adding a drop of nitric acid to the phosphoric acid after cooling, and then heating it again; a nitrate acts in the same way as nitric acid, as does chlorate of potash, except that with the latter the coloration is ephemeral. The violet product formed under these circumstances is the phosphate of sesquioxide of manganese, which has been isolated by the author in a pure state.

Arsenic acid behaves in the same way as phosphoric acid towards the compounds of manganese; but as the arseniate is decomposable

* See Chem. Gaz., 1853, p. 181.

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by heat, which is not the case with the phosphate, certain precautions are necessary with arsenic acid, and the two reagents cannot be substituted for each other. On these reactions in general the author has established processes for the recognition of the oxides and salts of manganese, the nitrates, chlorates, phosphates, and arseniates, which he describes as follows.

Examination for the Superoxides of Manganese.—To ascertain the existence of a superoxide of manganese, a drop of syrupous phosphoric acid, or a small quantity of an acid phosphate or of phosphate of ammonia, which is decomposed by heat, is put into a porcelain capsule; the little fragment of substance to be tested is put upon it, and heat is applied by the spirit-lamp, when the violet coloration is produced immediately; $\frac{1}{10}$th milligrm. of substance is sufficient to produce a distinct result.

Examination for Protoxide of Manganese.—The substance to be tested is put upon a drop of phosphoric acid in the little capsule; on the application of heat no coloration is produced. A trace of nitric acid is then added, and heat is again applied, when the violet colour appears. The sensibility is as great as in the preceding case.

Examination for a Nitrate.—To this the preceding reaction may be applied. The substance supposed to be a nitrate is substituted for the nitric acid, to see whether the coloration is produced. By this reaction nitric acid may be detected in a few tenths of a milligramme of a nitrate.

Examination for a Chlorate.—A chlorate gives the same result as a nitrate. But the chloride which appears to form the residue in the first phases of the operation afterwards acts upon the sesquioxide, the colour disappears, and there is an evolution of chlorine.

Examination for Phosphoric Acid.—The substance is dissolved in nitric acid, a trace of a protosalt of manganese is added to it, the whole is carefully evaporated, and the colour appears. Nitric acid and the protosalt of manganese do not furnish this result, which requires a very minute trace of phosphate dissolved in a drop of nitric acid.

Examination for Arsenic.—The colour produced by arsenic acid is less permanent than that given by phosphoric acid, arsenic acid being decomposable by the action of a comparatively low temperature.

Sesquiphosphate of manganese, dissolved in phosphoric acid, may also serve for the detection of the presence of reducing agents, as the protophosphate may indicate oxidizing agents.

Foreign metals do not prevent the characteristic reaction of manganese; their presence necessitates the use of a larger quantity of nitric acid, if they be metals or metallic compounds capable of reducing sesquioxide of manganese.—*Comptes Rendus*, March 30, 1857, p. 677.

On the Detection of Picric Acid. By J. Otto.

The beer of a brewery in Brunswick was suspected of receiving its bitterness, not from hops, but from picric acid, which, as is well

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known, has been recommended by Dumoulin as a substitute for hops. This gave origin to a series of experiments on the detection of picric acid, the results of which have been given in detail in Dingler's Polytechnisches Journal. The following contains what may be interesting to chemists.

Two properties of picric acid are especially deserving of notice, its extraordinary colouring power, and its strong bitterness. An aqueous solution containing a millionth of acid, therefore a milligramme in the litre, or a drachm in 8000 pounds of water, still has a yellow colour, distinctly perceptible in a litre-bottle. A solution so diluted has no bitter taste; this first is distinctly presented by a solution containing five-millionths, or $\frac{1}{200,000}$th of the acid.

Picric acid readily gives a beautiful and permanent yellow colour to wool. If an inch of clean white woollen yarn be laid in the solution containing one-millionth of the acid, it acquires no colour even in 24 hours. But it very soon becomes yellow on the addition of a few drops of stronger acid, such as dilute sulphuric acid.

White woollen yarn furnishes a simple and certain means for the detection of picric acid in beer, as Vohl has already stated. The woollen yarn is put into the beer, and left therein for 24 hours. It is then taken out, washed with pure water, and also with some alcohol, and pressed strongly between bibulous paper. The woollen thread appears of a pure yellow colour, if the beer contained picric acid; $\frac{1}{400,000}$th of the acid may be detected in beer in this way with certainty. Sulphuric acid must not be added to the beer; it has a sufficiently acid reaction of itself to effect the coloration.

In pure beer the woollen yarn acquires a brownish gray tinge. This slight coloration is quite distinct from that produced by picric acid; the latter is always a perfectly pure yellow.

If the beer be warmed with the yarn in it, the colour produced by pure beer becomes stronger. Nor is there any use laying the coloured yarn in a solution of protochloride of tin, and then in dilute solution of soda, to cause the formation of the red, nitro-hæmatic acid. The slight coloration acquired by the yarn in pure beer becomes pure yellow in protochloride of tin. If wool, which is not too slightly coloured by picric, be heated with lime water, and a drop of solution of protochloride of tin be then added to it, a reddish precipitate is produced.—Liebig's *Annulen*, April 1857, p. 67.

On the Toxicological Investigation of Arsenic. By Dr. Blondlot.

The author's object is to show that in the destruction of the organic matters by the process of Danger and Flandin, besides the greater or less quantity of sulphuret of arsenic which may originate from the sulphuretted hydrogen engendered by putrefaction, the carbonization by sulphuric acid of itself constantly produces a considerable proportion which escapes analysis.

250 grms. of fresh bullock's lung were cut up into large pieces, and 100 grms. of concentrated sulphuric acid were added to them;

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when the whole was liquefied, 2 centigrms. of a filtered solution of arsenious acid were poured in. The rest of the operation being effected by the known process, a dry, friable charcoal was obtained; this was exhausted by boiling water. After ascertaining that the last washing waters collected separately furnished no trace of an arsenical ring in Marsh's apparatus, the author washed the coal again with ammoniacal water; this second solution being evaporated to dryness, the residue was treated when hot with concentrated nitric acid added in small quantities, and the dried residue, having been treated with boiling water, was put into Marsh's apparatus, when it soon produced a thick and extensive ring.

The conversion of the arsenic into sulphuret in this experiment is easily explained by supposing that in virtue of the affinity of sulphur for a metalloid, the arsenious and sulphuric acids, which, taken separately, would not be reduced to their radicals under the conditions of temperature of the operation, undergo, when in presence of carbon, the decomposition expressed by the following formula:—

$$AsO^3 + 3(SO^3) + C^6 = AsS^3 + 6CO^2.$$

From this it appears that in toxicological researches the sulphuric charcoal must not only be treated with boiling water, but that the sulphuret of arsenic formed must be removed from it by washing with ammonia, and converted into arsenic acid by nitric acid.—*Comptes Rendus*, June 8, 1857, p. 1222.

PROCEEDINGS OF SOCIETIES.

Royal Society.

May 7, 1857. (The Lord Wrottesley, President, in the Chair.)

"On the part which the Silicates of the Alkalies may play in the Metamorphism of Rocks." By T. Sterry Hunt, Esq., of the Geological Survey of Canada.

In my last communication to the Royal Society on the Metamorphic Silurian Strata of Canada, I endeavoured to show, from the results of analyses of the altered and unaltered rocks, that it is the reaction between the siliceous matters and the carbonates of lime, magnesia, and iron of the sedimentary deposits, which has given rise to the serpentines, talcs, pyroxenites, chlorites, and garnet rocks of the formation. I then cited the observation of Bischof that silica, even in the form of pulverized quartz, slowly decomposes these carbonates at a temperature of 212° F., with evolution of carbonic acid; the same author mentions that a solution of carbonate of soda has the power of dissolving quartz under similar conditions*. Desiring to verify these observations, I have since made the following experiments.

Colourless crystalline quartz was ignited, finely pulverized, and then boiled for an hour with a solution of its weight of perfectly pure carbonate of soda; the amount of silica thus dissolved was 1·5

* Bischof's Chem. and Phys. Geology, Eng. Edition, vol. i. p. 7.

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per cent. of the quartz, but on repeating the treatment of the same quartz with a second portion of the carbonate, only ·35 per cent. was dissolved. The object of this process was to remove any soluble silica, and the quartz thus purified was employed for the following experiments, which were performed in a vessel of platinum.

I. 1000 parts of quartz and 200 of carbonate of soda were boiled with water for ten hours, and the mixture was several times evaporated to dryness, and exposed for a few minutes to a temperature of about 300° F. The amount of silica taken into solution was 12 parts.

II. A hydrocarbonate of magnesia was prepared by mingling boiling solutions of sulphate of magnesia and carbonate of potash, the latter in excess; the precipitate was washed by boiling with successive portions of water. 1000 parts of quartz were mixed with about as much of this magnesian carbonate and boiled as above for ten hours. An excess of hydrochloric acid was then added, the whole evaporated to dryness, and the magnesian salt washed out with dilute acid. The residue was then boiled for a few minutes with carbonate of soda, and gave 33 parts of soluble silica.

III. A mixture of 1000 parts of quartz, 200 of carbonate of soda with water, and an excess of carbonate of magnesia was boiled for ten hours, and the residue, treated as in the last experiment, gave 148 parts of soluble silica. The alkaline liquid contained a little magnesia but no silica in solution. That the soluble silica was really combined with magnesia was shown by boiling the insoluble mixture with sal-ammoniac, which, dissolving the carbonate, left a large amount of magnesia with the silica. This silicate was readily decomposed by hydrochloric acid, the greater part of the silica separating in a pulverulent form.

The third experiment was suggested by some observations on the reactions of silicate of soda with earthy carbonates. Kuhlmann has remarked the power of carbonate of lime to abstract the silica from a boiling solution of soluble glass*, and it is known that alumina exerts a similar action. I have found that when artificial carbonate of magnesia in excess is boiled with a solution of silicate of soda, the latter is completely decomposed with the formation of carbonate of soda, and a silicate of magnesia which gelatinizes with acids; and I have long since described this reaction in the evaporation of alkaline mineral waters†. This mutual decomposition of carbonate of magnesia and silicate of soda, conjoined with the power of carbonate of soda to dissolve silica, leads to a curious result. If we boil for some hours a mixture of ignited silica, obtained from the decomposition of a silicate by an acid (and consequently readily soluble in an alkaline carbonate), with a small portion of carbonate of soda and an excess of hydrocarbonate of magnesia, we obtain a dense powder which contains all the silica united with magnesia, and may be boiled with carbonate

* Comptes Rendus de l'Acad. des Sciences, Dec. 3rd and Dec. 10th, 1855, where will be found many important observations on the alkaline silicates.

† Reports of the Geol. Survey of Canada, 1851–53–54.

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of soda and sal-ammoniac without decomposition. It is obvious from the above experiments that similar results may be obtained with quartz, although the process is much slower; it would doubtless be accelerated under pressure at a somewhat elevated temperature, which would enhance the solvent power of the alkaline carbonate.

Silicates of potash and soda are everywhere present in sedimentary rocks, where decomposing felspathic materials are seldom wanting, and these salts in the presence of a mixture of quartz and earthy carbonates, aided by a gentle heat, will serve to effect a union of the quartz with the earthy bases, eliminating carbonic acid. A small amount of alkali may thus, like a leaven, continue its operation indefinitely and change the character of a great mass of sedimentary rock. Such a process is not only a possible but a necessary result under the circumstances supposed, and we cannot, I think, doubt that alkaline silicates play a very important part in the metamorphism of sedimentary rocks, which are composed for the most part of earthy carbonates, with siliceous, aluminous, and felspathic materials*.

The direct action between the carbonates and silica must necessarily be limited by their mutual insolubility, and by the protecting influence of the first-formed portions of earthy silicate; but with the solvent action of a small portion of alkali which is changed from silicate to carbonate, and then back again to silicate, the only limit to the process would be the satisfying of the mutual affinities of the silica and the basic oxides present.

June 15, 1857. (The Lord Wrottesley, President, in the Chair.)

"On a new Mode of forming Triethylamine." By A. W. Hofmann, LL.D., F.R.S.

Researches on the constitution of the nitrogenous organic bases, which I zealously prosecuted some years ago, and the result of which were communicated to the Royal Society, have been, by circumstances, interrupted for some time. Nearly all the observations recorded in my communications refer to the primary or amidogen-bases, *i. e.* the compound ammonias, in which 1 equivalent of hydrogen is replaced by an organic molecule. Of the secondary and tertiary bases (imidogen- and nitrile-bases), *i. e.* the ammonias in which 2 or 3 equivalents of hydrogen are replaced, and of the fixed ammonium-bases, little more is known at present than their mode of formation and their composition.

On again taking up this subject lately, it appeared of paramount importance to search for new and, if possible, simpler methods of forming the secondary and tertiary bases.

Of the several experiments made for this purpose, on which I intend to report at another opportunity, I may be allowed even now to quote a result which appears to be capable of a more general application.

* It is well known that small portions of alkalies are seldom or never wanting in the earthy silicates, such as serpentine, talc, pyroxene, asbestus, epidote, idocrase, and even beryl and corundum. See the memoir of Kuhlmann already cited.

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One of the common methods of preparing the amidogen-bases, consists in treating cyanic ether with hydrate of potassa, a reaction which was first observed by Wurtz. To take a special case, cyanate of ethyle, when treated with hydrate of potassa, assimilates 2 equivalents of water and splits into ethylamine, which is set free, and carbonic acid, which is fixed by the alkali. An appropriate modification of this reaction appeared to afford a means of passing directly from cyanate of ethyle to *triethylamine*. For this purpose it was only necessary to offer to the cyanate of ethyle 2 equivalents of oxide of ethyle instead of 2 equivalents of water. The action of cyanate of ethyle upon ethylic potassa appeared to involve the conditions necessary for accomplishing this result.

Experiment has fully confirmed this anticipation.

On digesting for several hours at a moderate temperature a mixture of pure cyanate of ethyle with pure ethylic potassa or soda (that is, absolute alcohol as far as possible, saturated with potassium or sodium), and distilling subsequently upon a sand-bath, a strongly alkaline liquid containing alcohol is obtained. Saturated with hydrochloric acid, this liquid furnishes on evaporation to dryness a residue from which a considerable quantity of *triethylamine* is expelled on addition of potassa.

The analogy of the two processes, of the formation of ethylamine and triethylamine, is obvious on glancing at the following equations.

$$\underset{\text{Cyanate of ethyle.}}{C_2ENO_2} + \underset{\text{Hydrate of potassa.}}{2(KO, HO)} = \underset{\text{Ethylamine.}}{N\begin{Bmatrix} E \\ H \\ H \end{Bmatrix}} + \underset{\text{Carbonate of potassium.}}{2KCO_3}$$

$$\underset{\text{Cyanate of ethyle.}}{C_2ENO_2} + \underset{\text{Ethylic potassa.}}{2(KO, EO)} = \underset{\text{Triethyl-amine.}}{N\begin{Bmatrix} E \\ E \\ E \end{Bmatrix}} + \underset{\text{Carbonate of potassium.}}{2KCO_3}$$

There could be no doubt regarding the identity of the basic compounds thus formed with triethylamine. The base floating on the surface of the saturated aqueous solution, possessed in a marked manner the characteristic odour of triethylamine. In order to exclude the possibility of a mistake, the hydrochloric solution of the compound was mixed with a solution of bichloride of platinum. Only after protracted standing of the highly concentrated solution, deep orange-coloured, well-formed crystals of the platinum-salt were deposited, the physical characters of which were still fresh in my memory.

The determination of platinum furnished results closely agreeing with the formula

$$N\begin{Bmatrix} E \\ E \\ E \end{Bmatrix} HCl,\ PtCl_2$$

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I have already applied this reaction in various directions, and shall communicate the results which I have obtained at a future period. On considering how frequently, in the action of hydrated potassa upon organic substances, the hydrogen of the water of hydration is assimilated by the products of decomposition, the substitution of ethylic potassa for the hydrate appears in many cases to promise valuable results from this mode of ethylation. The facility, however, with which ethylic potassa decomposes at a comparatively low temperature, must always be a serious obstacle to an extensive use of this reaction.

"Contribution towards the History of Thialdine." By A. W. Hofmann, LL.D., F.R.S.

Researches into the behaviour of several organic bases with bisulphide of carbon, which I intend to lay before the Society at a later period, have led to some experiments with thialdine, the results of which I may be allowed briefly to state, since they are but loosely connected with the principal object of the inquiry.

It appeared of interest to gain some insight into the constitution of thialdine, which is the prototype of an important class of alkaloids containing sulphur. To what group of bases does this body belong? Is it a primary, a secondary, or a tertiary base? The favourite method of questioning bases by means of iodide of methyle promised to furnish some elucidation of this subject.

Thialdine, dissolved in iodide of methyle, to which conveniently its own bulk of ether has been added, furnishes after twelve hours a solid crystalline mass, which may be readily freed from adhering thialdine by washing with ether and recrystallizing from alcohol.

The crystalline compound produced in this manner is the iodide of a methylated base, generated, as proved by analysis, by the union of equal equivalents of the two constituents.

$$\underbrace{C_{12}H_{13}NS_4}_{\text{Thialdine.}} + \underbrace{C_2H_3I}_{\text{Iodide of methyle.}} = \underbrace{C_{14}H_{16}NS_4I}_{\text{Iodide of methylthialdine.}}$$

The deportment of the new iodide resembles that of iodide of tetramethylammonium, and the analogous iodides, which I have described some years ago. Insoluble in ether, soluble in alcohol, and precipitated from this solution by ether in the crystalline state, soluble in water with an acid reaction, and separated from it again, unchanged by potassa in the cold, this substance exhibits in general all the characters which distinguish the iodides of the so-called ammonium-bases.

The great mobility of the elements in thialdine, and especially the large amount of sulphur which it contains, afforded but little hope of successfully submitting the new iodide to the experiment with oxide of silver, which is so characteristic for the ammonium-bases. On adding oxide of silver to the aqueous solution of this

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body, which, as has been remarked already, possesses an acid reaction, iodide of silver is formed, and the liquid assumes at once a marked alkaline reaction; but since the almost simultaneous formation of sulphide of silver, and a powerful evolution of aldehyde, sufficiently indicate the perfect destruction of the compound, and since experiment denotes the presence of ammonia in the liquid, it is impossible to decide whether the alkaline reaction observed after decomposition is due to the liberation of an ephemeral ammonium-base, or to its product of decomposition.

My experiments appear nevertheless to establish that thialdine belongs to the tertiary bases,—that it is a nitrile-base.

$$\text{Ammonia } N \left\{ \begin{matrix} H \\ H \\ H \end{matrix} \right.$$

$$\text{Thialdine } N \left\{ C_{12} H_{13} S_4. \right.$$

To the complex molecule, $C_{12} H_{13} S_4$, we must ascribe the faculty of replacing the 3 equivalents of hydrogen in the ammonia. In what manner, however, the elements are grouped in this complex molecule, whether we have here to assume a very unstable tribasic radical, or whether special molecules are inserted for each of the hydrogen-equivalents in the ammonia;—to decide these points further experiments are required.

Liebig and Wöhler, in their memoir on thialdine, state that the whole of the nitrogen of this base is eliminated in the form of ammonia, if the compound be decomposed by nitrate of silver. This deportment appeared to furnish an easy mode of controlling the formula of methylthialdine; after the decomposition of this body by nitrate of silver, I expected to find the whole of the nitrogen in the residuary liquid in the form of methylamine. On performing the experiment, it was found that the liquid contained considerable quantities of ammonia, but together with the latter alkali a fixed base. This unexpected deportment reminded me of experiments published several years ago *, on the action of oxide of silver on thialdine, which is said to be thus converted into *leucine*. The question presented itself, were the phenomena observed in the present case of an analogous character? had the above experiment given rise to the formation of methylated *leucine*?

Experiment proved that the decomposition of iodide of methylthialdine by oxide of silver gives rise to the formation of ammonia and of the oxide of tetramethylammonium

$$\left. \begin{matrix} C_2 H_3 \\ C_2 H_3 \\ C_2 H_3 \\ C_2 H_3 \end{matrix} \right\} NO, HO,$$

which was satisfactorily identified by the analysis of the gold- and platinum-compound.

* Goessmann, *Chem. Gaz.* vol. xii. p. 325.

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The following equation represents this change:—

$$\underbrace{4C_{14}H_{16}NS_4I}_{\text{Iodide of methyl-thialdine.}} + 20AgO + 2HO = 4AgI + 16AgS + \underbrace{12C_4H_4O_2}_{\text{Aldehyde.}}$$

$$+ 3H_3N + \underbrace{C_8H_{12}NO,HO}_{\text{Hydrate of the oxide of tetramethylammonium.}}$$

The absence of any leucine-like compound among the products of decomposition of iodide of methylthialdine induced me to repeat the experiment on the action of oxide of silver upon thialdine itself.

The transformation of thialdine into leucine, announced several years ago, and apparently very intelligible by the analogy of the formulæ of the two bodies

$$\begin{aligned} &\text{Thialdine} \ldots\ldots\ C_{12}H_{13}NS_4 \\ &\text{Leucine} \ldots\ldots\ C_{12}H_{13}NO_4, \end{aligned}$$

has not failed to rivet the attention of chemists. I wonder how such an error could have crept into science; for I have convinced myself, by a series of careful experiments, that this assertion is without the slightest foundation.

Thialdine, when treated with oxide of silver, as might have been expected, undergoes the same decomposition which Liebig and Wöhler had effected by means of nitrate of silver. It furnishes in this process aldehyde, acetic acid, and ammonia, but *no leucine*.

In conclusion, a remark which refers to a question connected with this alleged formation of leucine:—Soon after the statement regarding this subject had been made, Wagner* observed that the action of bisulphide of carbon upon amylamine gives rise to the formation of a crystalline compound. This compound was not analysed, but Wagner suggested that possibly it might be thialdine,

$$\underset{\text{Amylamine.}}{C_{10}H_{13}N} + 2CS_2 = \underset{\text{Thialdine.}}{C_{12}H_{13}NS_4},$$

and that in case this assumption proved to be correct, the action of bisulphide of carbon upon the homologues of ammonia might lead to the artificial formation, not only of leucine, but of glycocine, alanine, &c.

During my experiments on the deportment of bisulphide of carbon with organic bases, I have also had occasion to study the compound of amylamine with bisulphide of carbon. It is only necessary superficially to compare this substance with thialdine, in order to perceive at once that they are two absolutely different compounds; and if there is still a chance of producing leucine from amylamine, it is because the action of bisulphide of carbon does *not* give rise to the formation of thialdine.

* Journal für praktische Chemie, lxi. 505.

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THE CHEMICAL GAZETTE.

No. CCCLVI.—August 15, 1857.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Inverse Substitutions. *By* M. BERTHELOT.

CHEMISTS have learnt how to replace the hydrogen of organic substances by chlorine, bromine, or iodine, but there are as yet but few cases in which they can solve the opposite problem, which consists in regenerating the primitive compound from of the metamorphosed compound.

For this purpose four processes have been employed.

1. Melsens has changed chloracetic acid, $C^4 HCl^3 O^4$, into acetic acid, $C^4 H^4 O^4$, and perchloride of carbon, $C^2 Cl^4$, into marsh-gas, $C^2 H^4$, by the simultaneous action of water and amalgam of potassium, but an analogous conversion did not take place with the chlorinated derivatives of hydrochloric æther. The employment of the amalgam of potassium appears only to be applicable to chlorinated bodies which are easily decomposed; in other cases it acts exclusively upon the water.

2. Kolbe has also replaced the chlorine of chloracetic acid by hydrogen; he operated with the pile, employing zinc as an electrode. By the same process he has caused a similar substitution in a very curious series of peculiar acids, derived from the action of chlorine upon sulphuret of carbon. The pile can only act upon compounds which are soluble in water or in a conducting liquid.

3. The hydriodic æthers, $C^4 H^5 I$, $C^2 H^3 I$, $C^6 H^5 I$, when acted upon by zinc or sodium at a high temperature, lose their iodine without substitution, and furnish the hydrocarbons known as *æthyle*, $C^4 H^5$, *methyle*, $C^2 H^3$, *allyle*, $C^6 H^5$, &c. In operating with zinc in the presence of water, peculiar hydrocarbons are formed, in which the iodine of the hydriodic æther is replaced by hydrogen; namely hydruret of æthyle, $C^4 H^6$; marsh-gas, $C^2 H^4$; propylene, $C^6 H^6$. This is the most general known example of inverse substitution, and its discovery is due to Frankland.

4. In the researches upon iodized propylene, made by the author and De Luca, the iodine was replaced by hydrogen, by means of a peculiar process, which is further developed in the present memoir.

This process consists in the simultaneous action of mercury and muriatic acid upon iodized propylene, $C^6 H^5 I$; the result of which, even in the cold, is the formation of propylene, $C^6 H^6$, and of iodide

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supernatant liquid perfectly clear. They are then filtered through and chloride of mercury, bodies none of which would have been produced in the cold by the action of any two of the above agents; they originate from the simultaneous concourse of several affinities assisted by each other, nearly as the chlorides of silicium and boron are produced in the simultaneous reaction of chlorine, carbon, and silicic or boracic acids, no two of which have any reciprocal action.

The author has been led by his investigations upon the synthesis of the hydrocarbons, to study inverse substitutions in general. In all cases he has succeeded by various methods, either in substituting hydrogen for the chlorine, iodine, and especially bromine in hydrocarbons modified by substitution, or in regenerating the original carburets after they have undergone the action of those bodies. His processes depend sometimes on the use of free hydrogen at a high temperature, and sometimes on the concourse of two simultaneous affinities, equivalent to the employment of nascent hydrogen. In the latter case time is an essential element of the phænomenon.

I. *Free Hydrogen.*—Free hydrogen combines with the chlorine of chlorides of carbon towards a red heat; at the same time the hydrocarbon corresponding with the chloride of carbon experimented on is regenerated. A portion is destroyed by the heat, but a portion persists and may be collected. This process is only applicable to very stable compounds, but for this very reason it is suitable to compounds in which all the hydrogen may be replaced by chlorine, which denotes great stability both in the original hydrocarbon and in the chloride derived from it.

In these circumstances, protochloride of carbon, $C^4 Cl^4$, and the sesquichloride, $C^4 Cl^6$, furnish a considerable quantity of olefiant gas, $C^4 H^4$:—

$$C^4 Cl^4 + 8H = C^4 H^4 + 4HCl,$$
$$C^4 Cl^6 + 10H = C^4 H^4 + 6HCl.$$

Perchloride of carbon, $C^2 Cl^4$, produced marsh-gas, $C^2 H^4$, and olefiant gas. The marsh-gas is the result of an inverse substitution,—

$$C^2 Cl^4 + 8H = C^2 H^4 + 4HCl.$$

The olefiant gas appears to originate from the well-known decomposition in which perchloride of carbon, when heated to redness, forms chlorine and protochloride of carbon, $2C^2 Cl^4 = C^4 Cl^4 + 4Cl^4$.

The chloride of carbon, $C^{20} Cl^8$ (perchlorinated naphthaline), reproduced naphthaline at a bright red heat,—

$$C^{20} Cl^8 + 16H = C^{20} H^8 + 8HCl.$$

The chloride of Julin $(C^2Cl)^x$, reproduced, in large quantity, a crystalline body presenting the characters of naphthaline; no perceptible formation of a gaseous hydrocarbon took place at the same time. By this property, as well as by its odour and relative fixity, the chloride of Julin appears to be removed from the series of olefiant gas, to which it has hitherto been referred, and approximated to that of naphthaline. It is probably a chloride of perchlorinated

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naphthaline, $C^{20}Cl^{10} = C^{20}Cl^{8} + Cl^{2}$. This body, which possesses great stability, appears to be one of the ultimate products of the decomposition of the chlorides of carbon, just as naphthaline is one of the ultimate products of decomposition of the hydrurets of carbon. This accords with the ideas of substitution which imply a certain analogy of grouping between these two series of compounds.

The chloride of Julin, the perchloride, the sesquichloride, and the protochloride of carbon employed in the preceding experiments, were prepared by Kolbe's process by means of chlorine and sulphuret of carbon. These results, therefore, furnish a new means of producing olefiant gas, marsh-gas and naphthaline from their simple constituent bodies.

II. *Nascent Hydrogen.*—Having isolated the alcoholic hydrocarbons in the form of bromides, the author made various attempts to regenerate each of the hydrocarbons in order to study it separately. He first tried isolated metals, such as sodium, zinc, copper, and mercury. But these bodies, heated to 212°, 392°, and 572° F. with bromide of æthylene, $C^{4}H^{4}Br^{2}$, do not regenerate olefiant gas, $C^{4}H^{4}$, in noticeable proportion; the most they do is to form monobrominated æthylene, $C^{4}H^{3}Br$.

Zinc, heated to 572° F. with water and bromide of æthylene, regenerates olefiant gas, but the substitution is usually incomplete, and the gas is mixed with a very large quantity of free hydrogen, which renders the opening of the tubes dangerous. The free hydrogen is produced by the decomposition of the water by the zinc, which takes place simultaneously with, but independent of, the desired reaction. This is an unfavourable circumstance, as it usually opposes complete substitution, the decomposition of the water being completed before that of the brominated compound. The author, therefore, turned to the metals which do not of themselves decompose water.

Mercury, tin, lead, and copper were tried by turns, in presence of water, potash, and muriatic acid; copper, in presence of pure water, gave the best results. Bromide of æthylene, heated to 527° F. with water and copper, loses its bromine, and furnishes olefiant gas mixed with a certain proportion of hydrogen and with small quantities of oxide of carbon and hydruret of æthyle; but this reaction is extremely slow, only becoming complete after 30 or 40 hours of contact. To hasten the reaction, the author availed himself of the well-known instability of iodide of æthylene. For this purpose he caused the simultaneous reaction, at the above temperature, of bromide of æthylene, copper, water, and iodide of potassium. The reaction was completed in from 12 to 15 hours. It gives rise to olefiant gas, mixed with a little hydruret of æthyle, and usually with hydrogen, oxide of carbon, and even carbonic acid.

When the copper was omitted, the bromide of æthylene was still decomposed, a portion of the iodine of the iodide of potassium being set free, but the gas produced consisted principally of hydruret of æthyle, $C^{4}H^{6}$, mixed with a variable proportion of olefiant gas, carbonic acid, and often hydrogen and oxide of carbon. Thus,

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under the influence of water and iodide of potassium, the bromine of bromide of æthylene is replaced by hydrogen, a singular result, which, however, appears to be due to causes analogous to those acting in the preceding reactions.—*Comptes Rendus*, June 15, 1857, p. 1246.

On Ilixanthine and Ilicic Acid in the leaves of Ilex aquifolium. *By* Dr. F. Moldenhauer.

If the leaves of the Holly be extracted with alcohol of spec. grav. 0·863, the alcohol distilled off from the green tincture, the latter allowed to cool and filtered, and the filtrate set aside for several days, a granular sediment of insignificant appearance is formed in it. When crushed, the individual granules break up into a quantity of pale-yellow needles, to which various foreign matters adhere. To purify this crystalline substance, the sediment separated from the brown liquid was dried, treated with æther to get rid of adherent chlorophyll, and dissolved again in alcohol, when the yellow substance was separated by evaporating the alcohol and adding water; lastly, it was recrystallized from hot water, and the purity and uniformity of the preparation ascertained by the microscope. In this way a chemical compound was separated from the above leaves, possessing the general properties of a yellow colouring matter, to which the author gives the name of

Ilixanthine.—It was obtained from about 2 pounds of Holly leaves, and its preparation was only once performed from a deficiency of leaves. Leaves which had been collected in winter only furnished traces of this substance; those gathered in August contain it in abundance, but do not furnish the whole quantity which they contain by the above treatment. The remainder is obtained when the brown fluid in which the ilixanthine has been deposited is evaporated to a syrup, and dissolved in absolute alcohol, the yellowish-brown solution again evaporated, then dissolved in water, and finally precipitated by basic acetate of lead. The beautiful yellow precipitate was washed, suspended in water, and decomposed by sulphuretted hydrogen; then heated to boiling, and filtered whilst hot. The filtrate deposited no ilixanthine on cooling, but did so when evaporated to the consistence of a syrup and put by for about eight days. The scattered yellow granules contained in it were separated from the thick fluid in the usual way, washed with cold water, and recrystallized from hot water.

Ilixanthine possesses the following characters. It is a non-nitrogenous compound of a straw-yellow colour, separating in microscopic acicular crystals. When enclosed in a tube and heated in the oil-bath, a change of colour took place at 365° F.; at 370° F. it acquired a shining surface, and whilst the thermometer rose to 388° F., it fused to a transparent reddish-yellow drop, which remained exactly the same externally on cooling. When heated to 419° F., it began to boil, which appears to be in consequence of decomposition. It could not be sublimed either in a porcelain

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crucible, or between two watch-glasses; a coating of water was observed, which was certainly of a yellowish colour, but no undecomposed sublimed colouring matter could be distinguished. Ilixanthine is insoluble in æther, but soluble in alcohol. Cold water takes up little if any of it, but hot water dissolves it pretty readily, and deposits the colouring matter again on cooling in a perfectly crystalline form. The hot aqueous solution is yellow, and becomes orange-coloured with caustic alkalies or alkaline carbonates; neutral and basic acetate of lead precipitate therefrom beautiful yellow lakes, which dissolve in acetic acid to form a nearly colourless fluid. Copper salts produce no precipitate, nor do protosalts of iron; perchloride of iron produces a chlorophyll-green colour in the solution, without giving origin to a precipitate. When boiled with an alkaline solution of tartrate of copper no separation of protoxide of copper appeared, even after several hours. The yellow aqueous solution mixed with sulphuric acid lost its colour almost entirely; when this acid solution is boiled for some time, and left to cool, the colouring matter separates again in a crystalline form, and to all appearance unchanged. Concentrated muriatic acid, especially when hot, dissolves the colouring matter readily, with a yellow colour. It is also well adapted for dyeing stuffs mordanted with alumina or iron, and is but little inferior to quercitrine in the same circumstances. The decoction of the leaves gives satisfactory results as regards the dyeing properties.

The substance was burnt with chromate of lead. It was completely dried in warm sand under the air-pump, without having undergone any change. The analysis gave,—

	Found.		Calculated.
C	50·39	34	50·75
H	5·64	22	5·47
O	43·97	22	43·78

The formula therefore is $C^{34} H^{22} O^{22}$, or more simply, $C^{17} H^{11} O^{11}$.

The author also prepared an aqueous decoction of 4 pounds of dried leaves collected at the period of their fullest evolution in the beginning of August, for the purpose of repeating Stenhouse's experiment for the detection of theine. The decoction was precipitated by basic acetate of lead, and filtered; the filtrate was treated with sulphuretted hydrogen, evaporated to a syrup, and then placed in the cold for 24 hours. In this time nothing crystalline had separated from the very dark syrup. To remove the colouring substance, it was again diluted with water and heated with hydrated oxide of lead. The solution was filtered, and the small quantity of lead contained in it precipitated by sulphuretted hydrogen; it was then evaporated, and furnished a honey-yellow syrup, containing an abundance of sugar, which exactly resembled grape-sugar in its behaviour with sulphuric acid and with tartrate of copper and potash. This syrup was left to itself for some days, when a crystallization was produced, and the syrup resembled a crystallized honey. The microscope showed a mass of small crystalline laminæ grouped in fans,

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which were decidedly not theine. By filtration, pressure, solution in water, precipitation with alcohol, treatment with animal charcoal, and recrystallization, they were obtained colourless, and always crystallized in the same way. When heated in the platinum capsule, this substance became strongly inflated and burnt, leaving a dazzling white ash consisting entirely of lime. It soon appeared that this compound was the lime-salt of an organic acid. The amount of lime in the salt, completely dried at 212° F., is 18 per cent.

The determination of the lime consumed more than half the salt; the small residue served for the investigation of the principal properties of the salt and the acid. The salt was very soluble in water, but insoluble in alcohol. No precipitates or traces of the formation of a difficultly soluble salt were obtained with the neutral salts of silver, copper, iron, manganese, or zinc. Protochloride of tin and neutral and basic acetate of lead produced precipitates. The lead precipitates dissolved again in a great excess of the precipitant. The lead salt was decomposed by SH, and the filtrate evaporated, when a syrupous, colourless acid, something like malic acid, was obtained, in which, after some time, small crystalline laminæ were found, which exhibited a play of colours in polarized light. They appeared very similar to the lime-salt, and lime was found in them, so that the acid was not perfectly pure. The acid was converted into the baryta-salt by saturation with carbonate of baryta, which was effected with effervescence. This salt was still more soluble than the lime-salt; it could not be crystallized, but always dried into a mass like gum-arabic. To this acid the author gives the provisional name of *ilicic acid*.

The precipitate produced by basic acetate of lead in the aqueous decoction, was diffused in water and decomposed by SH. The fluid standing over the sulphuret of lead acquired a strong brown colour, and when evaporated left an acid extract. This contained an abundance of phosphoric acid, with some sulphuric acid, ilixanthine, and ilicic acid. The two latter substances could be separated from this extract, although in but small quantity.

Leaves collected in January furnished scarcely traces of ilixanthine; ilicic acid occurred in larger quantity, but accompanied by such quantities of gum-like matters, which presented a delusive resemblance to ilicic acid, that the author could not separate the acid from them.

The leaves are best collected in August. From the alcoholic extract, ilicine, which is still so little known, may be prepared more or less pure, when the brown liquid obtained after the distillation of the alcohol and filtration of the residue is precipitated by basic acetate of lead, the yellow precipitate washed, suspended in water, decomposed by SH, decocted, and filtered whilst hot, and the sulphuret of lead left upon the filter extracted with alcohol. The alcohol dissolves a dark yellowish-brown, tannin-like substance of very bitter taste, which is but slightly soluble in water, although sufficiently so to communicate the bitter taste to the latter.—Liebig's *Annalen*, June 1857, p. 346.

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Investigations on the Action of Chlorine upon Alcohol.

By A. LIEBEN.

A current of chlorine was passed through alcohol of spec. gra 0·863, care being taken to prevent any elevation of temperature. The acid liquid was agitated with a moderately concentrated solution of chloride of calcium, when *chloralcoholic oil* separated, which was dehydrated by chloride of calcium and submitted to fractional distillation. The principal product was a liquid boiling between 338° and 375° F. When purified by redistillations, this liquid formed an oil insoluble in water, possessing an agreeable aromatic odour, with a density of 1·1383 at 57° F., unattackable by a solution of caustic potash, and burning with a luminous, smoky flame, margined with green. Its composition is represented by the formula

$$C^{12} H^{12} Cl^2 O^4.$$

This formula was verified by the density of the vapour, which was found to be 6·45. The theoretical density corresponding with 4 volumes of vapour would be =6·46. The formula $C^{12} H^{12} Cl^2 O^4$, and the mode of production of this body, allow it to be regarded as *bichlorinated acetal*, $\left\{ \begin{matrix} C^4 H^2 Cl^2 \\ (C^4 H^5)^2 \end{matrix} \right\} O^4$.

The portions of liquid boiling below 338° F., were united and treated with a hot solution of caustic potash; an oil separated, which, when purified by fractional distillation, had the following properties:—an agreeable ætherial odour, a density of 1·0195, a density of vapour = 5·38, and a boiling-point between 302° and 320° F. Its composition is represented by the formula

$$C^{12} H^{13} Cl O^4,$$

which represents *monochlorinated acetal*, $\left\{ \begin{matrix} C^4 H^3 Cl \\ (C^4 H^5)^2 \end{matrix} \right\} O^4$.

From this it follows that the chlorinated derivatives of acetal are the principal elements of chloralcoholic oil. To ascertain whether a modification of the conditions would give rise to other analogous products, the author varied the degree of concentration of the alcohol employed.

Eighteen years ago M. Dumas made some experiments on the action of chlorine upon very concentrated alcohol, and obtained a body the analysis of which agrees exactly with the formula

$$C^{12} H^{11} Cl^3 O^4,$$

which represents *trichlorinated acetal*, $\left\{ \begin{matrix} C^4 HCl^3 \\ (C^4 H^5)^2 \end{matrix} \right\} O^4$.

In the reaction of chlorine upon very dilute alcohol, of which the temperature is raised, aldehyde, formic æther, acetic æther, acetal, and monochlorinated acetal distill over. Stas has already proved the presence of acetal amongst the products of the action of chlorine upon alcohol. The acid residue, besides muriatic acid, contains a small quantity of a non-volatile acid, which appears to be glycolic acid.

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Thus, by the action of chlorine upon alcohol, there are formed besides aldehyde, acetal and acetals gradually becoming richer in chlorine, in proportion as the concentration of the alcohol is increased. The formation of these chlorinated products, and finally of chloral, follows a certain progression which is represented by the following equations:—

$C^4 H^6 O^2 + 2Cl = 2HCl + C^4 H^4 O^2$, aldehyde,
$C^4 H^4 O^2 + 2C^4 H^6 O^2 = 2HO + C^{12} H^{14} O^4$, acetal,
$C^{12} H^{14} O^4 + 2Cl = HCl + C^{12} H^{13} Cl O^4$, monochlorinated acetal,
$C^{12} H^{13} Cl O^4 + 2Cl = HCl + C^{12} H^{12} Cl^2 O^4$, bichlorinated acetal,
$C^{12} H^{12} Cl^2 O^4 + 2Cl = HCl + C^{12} H^{11} Cl^3 O^4$, trichlorinated acetal,
$C^{12} H^{11} Cl^3 O^4 + 2HCl = 2HO + 2C^4 H^5 Cl + C^4 HCl^3 O^2$, chloral.

There exists between trichlorinated acetal and chloral, the same relation as between acetal and aldehyde.—*Comptes Rendus*, June 29, 1857, p. 1345.

Note on the Valuable Matter of Stable Manure. *By* P. THENARD.

In a previous memoir the author stated that certain elements of the soil, such as alumina, oxide of iron, and carbonate of lime, fix the valuable matter of fermented dung, by uniting with it to form compounds, which being slowly decomposed, furnish plants with an important portion of useful elements. This matter possesses a very high equivalent, and is capable of being split up in a great many ways. The author has found it not only in soils long since manured, but also in those which had never been manured, so that it would seem to be produced spontaneously in the soil; it is the slowness or rapidity of its reproduction which causes the difference in the quality of soils, and lastly, it is the principal and powerful element of those valuable soils, which may be constantly cropped, without manuring.

The extraction of this matter is effected by the following process. When fermented dung is treated with water a brown solution is obtained. The brown matter consists principally of a compound of ammonia with a peculiar nitrogenized acid; by treating it with a strong acid (such as muriatic acid), the organic acid is isolated, and as it is insoluble in water, it is precipitated immediately. In this state it is gelatinous and occupies a great volume; its washing would consequently be difficult, if it did not coagulate by boiling. It is very impure at first, and to purify it, must be dissolved in ammonia as many as ten times, precipitated by an acid, washed rapidly with boiling water, and dried quickly under the air-pump. In this series of operations, the washing waters gradually become colourless, and the acid, which at first contained only 3·5 per cent. of nitrogen, and left several hundredths of ash, contains at last 5·5 per cent. of nitrogen, and only gives 1 to 2-thousandths of ash. The same results are obtained if dilute potash be substituted for the ammonia, so that the gain in nitrogen cannot be derived from the ammonia in consequence of imperfect washing. This acid, which pos-

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sesses a great part of the properties of proteic acid, the author calls *fumic acid.*

When it is dry and in fragments it closely resembles good coal; it is amorphous, black, with a brilliant fracture, and has the density and hardness of coal; when calcined in a muffle, it burns with a large and very luminous flame, leaving a carbonaceous residue, comparable to coke. It is completely insoluble in water; æther and alcohol scarcely dissolve some traces of it; with the exception of potash, soda, and ammonia, bases form with it insoluble salts, which resemble it in colour. Its analysis gave,—carbon, 60·5; hydrogen, 5·1; nitrogen, 5·5; oxygen and sulphur, 29. This gives the formula

$$C^{30}H^{15}NO^{11};$$

but the author does not guarantee the exactitude of this formula, as the salts always present variable quantities of base.

Neutral fumate of ammonia forms compounds directly with alumina and oxide of iron. In the cold, carbonate of lime has no action upon it, but in course of time, or by ebullition, the fumate of ammonia becomes decomposed into fumate of lime which remains, and carbonate of ammonia which is volatilized. The liquid becomes colourless. Bicarbonate of lime, even in presence of a great excess of carbonic acid, instantly precipitates fumate of ammonia; and there is an exchange of bases and acids. The same is the case with all the soluble salts of lime.

If the fumate of ammonia have an excess of base, the neutral salts of alumina do not precipitate it at once, but a few drops of chloride of sodium instantly cause precipitation. The same is the case with an acid solution of phosphate of alumina; and when this body, so insoluble in the presence of alkalies, is seen to remain in solution in basic fumate of ammonia, is there not reason to draw some induction to explain the passage of phosphoric acid into plants?

The combined action of water and air, especially in presence of clay, which has no reaction of its own, rapidly alters the neutral fumate of ammonia; it soon becomes very acid to test-papers. Fungi form on the surface of the liquid, and a soluble coloured acid is produced, which did not previously exist. This may be the acid of those soils, which, without being boggy, nevertheless produce rushes and other aquatic plants. In soils of this discription the author has found considerable quantities of an acid of the same kind.

The author has studied some products of substitution of fumic acid. If recently precipitated fumic acid, suspended in water, be treated with chlorine, instead of dark-brown it becomes orange-yellow. When washed and dried, the new substance is trichlorinated fumic acid. In analysing this substance and determining its chlorine, the author found sulphur in fumic acid. He cannot decide whether this is an impurity, or a constituent part of the acid, or whether it belongs to a peculiar, new body which he could not eliminate. Direct analyses only gave traces of sulphur; and, on the other hand, as the distillation of trichlorinated fumic acid furnishes an essence exactly

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analogous to oil of mustard in odour and taste, and the analysis was made under such conditions that this essence might be volatilized, the sulphur might have escaped in this way. However, at a heat of 212° F., trichlorinated fumic acid evolves muriatic acid; and if, instead of heating it dry, it be boiled in water, there remains in solution in this water a black substance, which is acid *per se*, and not by the muriatic acid which it contains, whilst at the bottom of the capsule there is a very insoluble substance of a tolerably bright chocolate-brown colour, which under the microscope appears amorphous, but granulated like very fine sand. This body, which contains 3·1 per cent. of nitrogen and 12 per cent. of chlorine instead of 23 contained in the trichlorinated acid, did not yield a trace of sulphur. It dissolves in alkalies, in which it again undergoes splitting, and two essentially different bodies, of which one is very soluble, are obtained. The reactions furnished by nitric acid with fumic acid are also numerous. But the most curious body is a yellow acid, having the aspect of a resin, which is slightly soluble in water, and when heated, is decomposed and gives products of the benzoic series; when the oxidation is carried further oxalic acid is obtained.—*Comptes Rendus*, May 11, 1857, p. 980.

On the Metals associated with Platinum.

By MM. H. Sainte-Claire Deville *and* H. Debray.

All the simple bodies of native platinum have a common physiognomy, and yet some of them possess intimate analogies with the most dissimilar bodies,—from osmium, which is a metalloid, to rhodium, a metal more noble than gold. Their common character is the marked tendency to revert to the metallic state under the most feeble influences,—the ready dissociation of the elements of their compounds.

Platinum.—Next to palladium it is the most fusible metal of the group. When once it has been fused, it becomes volatilized sensibly, and at the moment of solidification presents the phænomenon of spitting, which has not hitherto been observed except in silver. An oxide of platinum is therefore probably formed at a very high temperature, and destroyed when the metal cools. This theory of spitting is justified by an experiment made by exposing silver to a temperature far superior to that necessary for its vaporization. The silver becomes oxidized, smokes like a lead-bath, and when the vapours are rapidly condensed, they are found to consist of yellow oxide of silver, which forms a coating a little clearer than that of lead. The silver must be perfectly pure. Proust had previously remarked that silver became oxidized before the blowpipe.

To cause the spitting of platinum, a mass of 500 to 600 grms. of metal must be kept in fusion in lime for a long time, and the metallic bath must be suddenly uncovered. When it is allowed to cool slowly, the spitting does not take place.

The fusion of platinum in lime refines the metal very perfectly, and furnishes a metal as soft as pure copper. The metal is whiter

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than ordinary platinum, and it has lost all porosity. It nevertheless still retains the property of condensing gases at its surface and producing the phænomena of the flameless lamp; its density is 21·15.

Palladium.—The spitting of palladium is effected with even more facility than that of platinum. However, as the oxygen is only disengaged at the moment when the upper stratum of the metal solidifies, the ingot which has undergone this process is cavernous, although its surface may be perfectly regular. Palladium, which is nearly allied to silver, is perhaps more oxidizable than that metal; its surface is always tarnished by a slight coat of oxide. It volatilizes at a very high temperature, producing greenish vapours which condense into a bistre-coloured powder, a mixture of metal and oxide. Like silver it dissolves in hydriodic acid with evolution of hydrogen; like platinum and the metals of platinum in general (except perhaps ruthenium), palladium can produce the phænomena of the flameless lamp under certain conditions.

Osmium.—This substance, like arsenic which it so much resembles, is infusible under the ordinary pressure. But at a very high temperature it is rapidly volatilized without oxidation and without leaving a residue, if it be pure.

The temperature at which osmium disappears is not lower than that at which platinum emits vapours. Osmic acid boils towards 212° F. This curious property has allowed the density of its vapour to be determined. The experiment, which was twice tried at temperatures of 475° and 547° F., gave two nearly identical numbers, namely 8·89 and 8·87. From this the equivalent of osmic acid corresponds with 2 volumes of vapour. These numbers indicate besides that the equivalent of osmium must probably undergo a slight correction which would render it equal to the equivalent of platinum. In this operation the quantity of osmium reduced is insensible. A remarkable peculiarity is observed at the moment when the balloon is opened over the mercury. In contact with osmic acid mercury acquires the property of moistening glass, and the balloon is silvered with singular perfection by the osmium reduced by the mercury, or by an amalgam. The acid employed was prepared by the process of Berzelius, that is to say, by roasting osmium in a current of oxygen, an operation which readily furnishes considerable quantities of pure acid.

Rhodium.—Rhodium fuses with more difficulty than platinum; the same fire which is capable of liquefying 800 grms. of platinum, only fuses 40 to 50 grms. of rhodium in the same time. No indications of volatility were observed in this metal, but it becomes oxidized very superficially like palladium, and spits in the same way. The surface of the ingot is often bluish. When rhodium has been properly refined and freed from silicium and osmium by roasting in contact with lime, it has very remarkable physical properties. Less white and less brilliant than silver, it is equally ductile and malleable.

An alloy of platinum and rhodium with 30 per cent. of the latter, fused more readily than rhodium. After being fused and refined,

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this alloy works well and furnishes chemical vessels possessing the valuable property of being unattackable by nitromuriatic acid.

Iridium.—Iridium is the most refractory of all the metals of platinum; scarcely 10 grms. of iridium can be fused in the time necessary for the complete liquefaction of 100 to 150 grms. of platinum. After being fused and refined, iridium is still brittle, although it may be flattened a little under the hammer. It betrays no signs of volatility. It has the property of condensing gases at its surface, and is capable of serving for the experiment of the flameless lamp.

Ruthenium.—The authors have been unable to procure this metal in a sufficiently pure state. It appears that under the influence of high temperatures and in contact with lime, ruthenium disappears, producing a crystalline scoria, and leaving a very refractory and very heavy ingot, the density of which is at least 17, which appears to contain much iridium. In a future communication the authors will describe their methods for the extraction of these metals in the dry way.—*Comptes Rendus*, May 25, 1857, p. 1101.

Improved Mode of Preparation of Crystallized Silicium.

By Professor WÖHLER.

According to the process formerly described by me*, aluminium is fused with 20 to 40 times its weight of fluosilicate of soda at a good red heat. I have since found, however, that the latter salt may be dispensed with, and its tedious preparation avoided by fusing the aluminium in a Hessian crucible with 5 times its weight of soluble glass and 10 times its weight of crysolite, and keeping the mass in a fluid state for about half an hour. For this purpose I employ the beautiful fused soluble glass from the factory of M. Kuhlmann of Lille. This is powdered, and mixed with the powdered cryolite; the crucible is half-filled with the mixture, a piece of aluminium is laid upon it, and this is covered with the other half of the mixture. In this way dark iron-black reguli, completely saturated with silicium are obtained; their surface is generally covered with shining three- and six-sided laminæ of silicium.

It is remarkable that these masses of aluminium, containing silicium, are not fusible again at the temperature at which they were formed. A globule of this kind may be kept at a red heat for a long time in an open crucible, without fusing or becoming oxidized. If it be thrown whilst red-hot into cold water, about half the volume of aluminium, flows out as a coherent mass, which remains red-hot for a minute under the water; the silicium, however, remains in the form of the globule, as a ragged crystalline mass, filled with empty spaces. In the preparation of the silicium, therefore, it is advisable to treat the regulus in this way before solution in muriatic acid, as by this means much aluminium is regained, which, although it contains silicium, may be employed in fresh preparations.—Liebig's *Annalen*, June 1857, p. 382.

*Chem. Gaz. 1856, p. 91.

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ANALYTICAL CHEMISTRY.

On the Detection and Estimation of small Quantities of Arsenic in Combination with a large Excess of Copper. By FREDERICK FIELD, M.R.I.A., F.C.S.*

PROFESSOR BLOXAM has shown, in an elaborate paper published in the Quarterly Journal of the Chemical Society, vol. v. pp. 119–122, that when arsenic is present in minute proportions in alloys or mixtures of copper, that it cannot be separated by digesting the precipitated sulphides in the sulphides of ammonium or potassium. "No arsenic," observes that chemist, "was found in the sulphide of ammonium solution, in the analyses of mixtures containing respectively,—

	1·00	copper,
	0·01	arsenic,
and	0·90	copper,
	0·01	arsenic;
but when	0·50	copper
was present with	0·01	arsenic,

the latter metal was detected in the sulphide of ammonium solution, and was always found when smaller quantities of copper were present."

It appears, therefore, from these experiments, that when arsenic exists in the proportion of 1 per cent., it is entirely lost sight of in analyses, conducted by this method, provided copper constitute the remaining 99 per cent., and even 1 part in 90 also escapes detection. Whether the whole or only a portion of the arsenic is obtained when its proportion to copper is as 1 to 50, we are not informed. In copper metallurgy it is often of great importance, not only to detect, but also to estimate the arsenic that may be contained in rough copper and its sulphides, known technically as regulus, coarse metal, white metal, &c., as in certain processes in copper smelting, especially where calcination is not adopted, more or less arsenic is sure to be present in the copper or the regulus, according to the quantity originally existing in the cupriferous mineral. The following method may be found to be very advantageous for the detection of minute traces of arsenic, and unless that element occur in such very small proportions as to be unworthy of consideration, it has been invariably recognized.

According to Wackenroder (Gmelin's Handbook of Chemistry, vol. v. p. 412), "oxalic acid throws down from cupric salts, a pulverulent bluish-green precipitate, and even dilute solutions, containing excess of acid, are thrown down by oxalic acid." This is so far true, but oxalic acid will also throw down oxalate of copper from intensely acid solutions even at the boiling-point. By the careful addition of this reagent to copper dissolved in nitric acid, nearly all the metal is precipitated as oxalate, as the following results will show:—

* Communicated by the Author.

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10 grs. copper dissolved in great excess of nitric acid gave in the filtrate after addition of excess of oxalic acid ..... 0·068 copper.
10 grs. „ „ „ 0·057 „

A solution of arsenic acid affords no precipitate with oxalic acid.

It appears from this that more than 99 per cent. of copper can be removed by the addition of oxalic acid to acid solutions of the metal.

50·00 grs. of copper and 00·50 arsenious acid =·378 or ·756 per cent. arsenic, were boiled with excess of nitric acid until no more red fumes were evolved. Oxalic acid was added in slight excess, and the precipitate allowed to subside for two or three hours. On filtering the solution, which was colourless, so small a quantity of copper was present, that ammonia only caused a very slight blue tinge. Sulphide of ammonium imparted a brownish-black colour, and in a short time a black precipitate of sulphide of copper was deposited. This was filtered off and excess of hydrochloric acid added to the filtrate, which afforded on warming a copious precipitate of pentasulphide of arsenic mixed with sulphur. After digestion on the sand-bath for some time, it was filtered, dissolved in a small quantity of nitrohydrochloric acid, deoxidized by sulphurous acid, boiled, and allowed to cool. A stream of sulphuretted hydrogen precipitated pure tersulphide of arsenic. The quantity obtained was 0·600=0·365 arsenic. The quantity taken 0·378 arsenic.

Still smaller portions of arsenic were detected.

20·00 grs. of copper and 00·10 arsenious acid treated in the same manner gave a distinct yellow precipitate of pentasulphide.

40·00 grs. copper and 00·10 arsenious acid gave equally decisive results. It will be observed in this last experiment that the arsenic is only in the proportion of 00·189 per cent. Thus $\frac{1}{5}$ of the quantity, which by the usual method escapes observation, can be easily recognized by the employment of oxalic acid.

There is, however, one great practical difficulty in the application of this reagent, which it was feared would have proved fatal to the success of the process, and this is the great difficulty of filtering the precipitated oxalate from the arsenic in solution. The powder is so extremely fine, that, although double and even treble filters were employed, a portion of the precipitate passed through, and had to be again and again returned. After many experiments and failures, the following method was found to obviate the difficulty to a great extent. Ammonia was added to the nitric solutions of arsenic and copper until the oxide of the latter was precipitated, but not redissolved. Excess of oxalate of ammonia added until the whole was dissolved, forming a clear dark-blue solution of the double oxalate of copper and ammonium. Nitric or hydrochloric acid threw down from this the oxalate of copper in a powder which was easily filtered and washed; the precipitation of the copper by this means is still more complete. In some instances even sulphide of ammonium has failed to give any dark tinge, and on the addition of hydrochloric acid pure pentasulphide of arsenic precipitated. The separation, however, is very seldom so satisfactory.

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The copper can be readily estimated from its oxalate by desiccation of the latter, and subsequent ignition. Metallic copper is produced, which is instantaneously converted into the black oxide. Should the oxidation be incomplete, a few drops of nitric acid, evaporation and ignition will suffice. When it is desired to estimate the whole of the copper, the small quantity which has escaped precipitation by oxalic acid, and is subsequently thrown down by sulphide of potassium or ammonium, is dissolved in a little nitric acid, and the solution added to the oxide previous to its final ignition. The results are very perfect.

Oxalate of copper, when dried at any temperature under 212°, always contains water.

39·30 grs. after heating for some days at a temperature approaching 200° F., gave on ignition 18·50 CuO. Pure oxalate should have yielded 20·68 CuO. Probably it still contained an atom of water.

	Calculated.	Found.
Oxide of copper	18·49	18·50
Oxalic acid	16·63	
Water	4·18	
$CuO\,C^2O^3 + Aq$	39·30	

10 grs. heated to 250 gave 5·03 CuO. Calculation from the anhydrous oxalate should give 5·26 CuO.
5 grs. heated to 250 gave 2·53 CuO.
Calculated 2·63.

It is therefore safer always to ignite the oxalate before calculating the amount of copper or its oxide.

Coquimbo, Chile, June 16, 1857.

Determination of Morphine in Opium. *By* M. Fordos.

The quantity of morphine in the opiums of commerce may vary from 0 to 14 per cent., so that it becomes a matter of importance to know this amount before making use of opium for medical purposes. The author proposes the following process.

15 grms. of opium cut into thin slices are macerated in 60 grms. of water, and agitated from time to time. In twenty-four hours the product of maceration is put into a mortar, and powdered with the pestle. The whole is then poured upon a small filter, and when the liquid has run away, the filter is washed with 15 grms. of water, which have served to wash the mortar and the bottle in which the maceration took place. The washing is repeated a second and third time, with 10 grms. of water each time. The opium is then sufficiently exhausted.

A third of the liquid is taken to determine the quantity of ammonia necessary for the precipitation of the morphine. The ammonia is added drop by drop from a graduated burette; the addition is stopped the moment the liquid presents a slight ammoniacal odour, and the quantity of ammonia is noted.

The morphine is determined with the other two-thirds of the

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liquid, which represent 10 grms. of opium. To this portion its volume of alcohol of spec. grav. 0·848 is added, and a quantity of ammonia double that used in the first experiment. (A slight excess of ammonia must be added to effect the complete separation of the morphine.) The liquid is agitated and left to itself in a well-corked bottle. Crystals are soon deposited; some in fine, nearly colourless needles (narcotine); others in larger prisms, with a little more colour; these are morphine. In two or three days the bottle is shaken and again left for a few hours to allow the morphine to settle completely. The crystals are then collected on a small filter, and washed with 15 or 20 cub. cent. of very weak alcohol at 104° F.; this washing carries off the mother-liquors, and at the same time frees the crystals of the colouring matter which soils them. The filter retains slightly coloured crystals of morphine, and colourless crystals of narcotine. The filter is dried upon the funnel, and then 10 cub. cent. of pure sulphuric æther are poured upon the filter, followed by 10 or 15 cub. cent. of chloroform in two parts. The narcotine is instantly dissolved and carried off by the chloroform, which does not touch the morphine. Lastly, the filter is washed with 15 cub. cent. of æther to remove the last traces of chloroform and narcotine; the filter is dried, and the crystals of morphine, which easily detach, are weighed.

In this process the water dissolves all the morphine which exists in the opium in a state of saline combination, but very little narcotine and resinous and colouring matters. By adding ammonia to the aqueous solution, a precipitate of morphine, narcotine, and colouring matters is obtained. The addition of alcohol retards the precipitation of the alkaloid, and gives them time to acquire a crystalline form; whilst it retains the resinous and colouring matters in solution.—*Comptes Rendus*, June 15, 1857, p. 1256.

PROCEEDINGS OF SOCIETIES.

Royal Society.

June 15, 1857. (The Lord Wrottesley, President, in the Chair.)

"On the Action of Sulphuric Acid upon Anisic and Salicylic Acids." By A. W. Hofmann, LL.D., F.R.S.

In a paper read before the Royal Society*, we have, Mr. Buckton and myself, directed attention to the general occurrence of the disulpho-acids, of which only few and scattered examples were known at that time.

M. Louis Zervas has since continued the study of this subject in my laboratory, and has arrived at the following results.

Anisic acid, treated with Nordhausen sulphuric acid, at a temperature of 100°, assimilates the elements of 2 equivs. of sulphuric acid, and is converted into a crystalline acid, containing

$$C_{16}H_8O_6 + 2HSO_4 = C_{16}H_8S_2O_{12} + 2aq.$$

The formula of this acid, which M. Zervas calls *sulphanisic acid*,

* See Chem. Gaz. vol. xiv. p. 395.

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was controlled by the analysis of a crystalline lead-salt and a barium compound, which were found to contain respectively

Lead-salt .... $C_{16}(H_6Pb_2)O_{12}+2aq.$
Barium-salt .. $C_{16}(H_6Ba_2)O_{12}+2aq.$

If the mixture of anisic and fuming sulphuric acid be submitted to higher temperatures than that of boiling-water, a lively evolution of carbonic acid takes place, containing, if the temperature be maintained within the proper limits, scarcely a trace of sulphurous acid. After several hours' digestion, the solution contains no longer anisic or sulphanisic acid, but a new acid, which has the composition

$$C_{14}H_8S_4O_{14}.$$

The formula of this acid, which could not be obtained in a state fit for analysis, was fixed by the analysis of a barium-salt, which was found to contain

$$C_{14}(H_6Ba_2)S_4O_{14}+2aq.$$

This acid may be considered as formed by the association of 1 equivalent of anisol (the product of the action of alkaline earths upon anisic acid at a high temperature) with 4 equivalents of anhydrous sulphuric acid. M. Zervas has, in fact, experimentally proved, that his acid may be obtained directly by treating anisol with fuming sulphuric acid, and he accordingly proposes to designate this compound by the name of *disulphanisolic acid*.

From the preceding experiments it is obvious that the action of sulphuric acid upon organic acids with 6 equivalents of oxygen, is perfectly similar to that which this agent exerts upon acids with 4 equivalents of oxygen.

Acetic acid.

1st Stage .. $C_4H_4O_4+2HSO_4=C_4H_4S_2O_{10}+2HO.$
2nd Stage.. $C_4H_4O_4+4HSO_4=C_2H_4S_4O_{12}+4HO+2CO_2.$

Anisic acid.

1st Stage $C_{16}H_8O_6+2HSO_4=C_{16}H_8S_2O_{12}+2HO.$
2nd Stage $C_{16}H_8O_6+4HSO_4=C_{14}H_8S_4O_{14}+4HO+2CO_2.$

There can be no doubt that salicylic acid, so closely allied to anisic acid, in fact, its homologue, a step lower in the system, must exhibit a similar deportment. Mr. Baldwin Duppa has been occupied with this subject in my laboratory, and has already obtained the first term, the *sulpho-salicylic acid*,

$$C_{14}H_6S_2O_{12},$$

which forms extremely beautiful compounds.

On submitting salicylic acid to the action of an excess of sulphuric acid, at a temperature of 180°, the same phenomena present themselves which are noticed in the case of salicylic acid, a powerful evolution of carbonic acid ensues, and the solution now contains a new sulphur-acid, which is crystalline. As yet Mr. Duppa has not succeeded in obtaining this acid in a state of sufficient purity for analysis, but it may be assumed, without much hesitation, that it will be found to be

Disulphophenic acid.... $C_{12}H_6S_4O_{14}.$

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"On the Separation of Iodine, Bromine, and Chlorine, and the comparative degree of Affinity of these Elements for Silver; with some Analysis of their Combinations with that Metal occurring in Chili." By Frederick Field, Esq.

Although both bromide and iodide of silver are decomposed by the action of chlorine at an elevated temperature, yet chloride of silver is completely decomposed by bromide of potassium, and both the bromide and chloride of silver by iodide of potassium. Even the action of hot strong hydrochloric acid has but little influence upon the iodide of silver; many days of continuous boiling are necessary for its entire decomposition. I believe that it has been the opinion of chemists that chlorine possesses an affinity for silver superior to all other elementary bodies, and we are told in Gmelin's Handbook that all salts of silver, even the insoluble ones, are converted into chloride by solutions of metallic chlorides. From the following experiments it appears to me that bromine has a greater affinity for silver than chlorine, and iodine a still greater affinity than bromine.

When a mixed solution of bromide of potassium and chloride of sodium is added gradually to a solution of nitrate of silver, not in excess, no trace of chloride of silver is precipitated, as long as any bromide remains in solution.

If to a similar solution, iodide and bromide of potassium and chloride of sodium be added, iodide of silver and nitrate of potassa are formed, the bromide of potassium and chloride of sodium remaining undecomposed.

When bromide of potassium is poured upon chloride of silver, an entire decomposition ensues, bromide of silver and chloride of potassium being produced.

When iodide of potassium is added to chloride of silver, iodide of silver and chloride of potassium are formed; and when iodide of potassium is added to bromide of silver, there is a similar decomposition, the iodine replacing the bromine.

When chloride of silver in excess is agitated with a solution of iodide of potassium and warmed for some hours, no trace of iodine can be detected in the solution: when however chloride of sodium is poured upon iodide of silver, no decomposition occurs, neither is there any action upon bromide of silver with the same salt: and when bromide of potassium is added to iodide of silver, there is no alteration in the union of the elements.

From a number of experiments made in illustration of the preceding statements, I deemed it possible that the separation of chlorine, bromine and iodine could be accomplished by this reaction.

The method which I have devised is simply this: After weighing three equal portions of the salts to be analysed, they are placed in three flasks with ground-glass stoppers, and about an ounce of water is added to each; nitrate of silver being then added, slightly in excess, to the three, the stoppers are replaced, and each flask agitated violently. The precipitates subside in a few minutes, leaving the

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separate funnels, and washed with hot water. No. 1 is dried and weighed. No. 2 is digested in bromide of potassium, dried and weighed; and No. 3 in iodide of potassium, dried and weighed.

To test the method, a mixture was made of 5 grains of iodide of potassium, 5 grains of bromide of potassium, and 5 grains of chloride of sodium. The following is a comparison of the theoretical and experimental results:—

	EXPERIMENT.	THEORY.
Iodine	3·69	3·81
Bromine	3·51	3·34
Chlorine	2·92	3·02

I have availed myself of this method in analysing several silver ores containing chloride, bromide and iodide of silver found in Chili, the formulæ of which I subjoin:—

Chloride of silver	Ag Cl.
Chlorobromide of silver	2Ag Cl, Ag Br.
Chlorobromide of silver	3Ag Cl, 2Ag Br.
Chlorobromide of silver	Ag Cl, 3Ag Br.
Bromide of silver	Ag Br.
Iodide of silver	Ag I.

"Note on the Density of Ozone." By Thomas Andrews, M.D., F.R.S., Vice-President of Queen's College, Belfast, and P. G. Tait, M.A., Fellow of St. Peter's College, Cambridge, and Professor of Mathematics in Queen's College, Belfast.

It is known that ozone can only be obtained mixed with a large excess of oxygen. In a former communication by one of the authors of this note, it was shown that in the electrolysis of a mixture of 8 parts of water and 1 of sulphuric acid, the mean quantity of ozone does not exceed ·0041 gramme in a litre of oxygen, or $\frac{1}{350}$th part. By using a mixture of equal volumes of acid and water, the relative quantity of ozone may be doubled; but even with the ozone in this more concentrated state, the ordinary methods of determining the density of a gas are plainly inapplicable. The difficulty of the problem was farther increased by the rapid action of ozone on mercury, which rendered it impossible to collect or measure the gas over that metal; and the tension of aqueous vapour, as well as the gradual destruction of ozone by water, prevented the use of the latter. After numerous trials, the method finally employed was to measure the change of volume which occurs in exposing a gaseous mixture containing ozone to a temperature of 230° C., or upwards. The volume of the gas after this treatment was invariably found to have increased; and by eliminating the effects of alteration of temperature and pressure during the course of the experiment, by the aid of a similar vessel to that containing the ozone, the authors succeeded in estimating the change of volume which took place, to an extremely small fraction of the entire amount.

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The vessels employed in different experiments varied in capacity from 200 CC. to 600 CC., and terminated in tubes of about 2 millimetres in diameter, bent in a U-form and containing sulphuric acid. The amount of ozone was ascertained by passing a stream of the gas through two other vessels, one placed on each side of the vessel to be heated, and afterwards analysing their contents by the method described in the communication already referred to. It was easy to measure with certainty a change of pressure amounting to $\frac{1}{60,000}$th of the whole; but on account of the ordinary fluctuations of atmospheric pressure between two consecutive observations of the primary and auxiliary vessels, it was rarely possible to work to this degree of accuracy.

The experimental data have not yet been completely reduced, and some slight corrections have yet to be investigated; but the general result of the inquiry, which has been a very protracted one, gives—on the assumption that ozone is oxygen in an allotropic condition—for its density as compared with that of oxygen, nearly the ratio of 4 to 1.

The following approximate formulæ were employed in the reduction of the experiments. They are sufficiently exact for the purpose of calculation on account of the smallness of the quantities observed.

I. To reduce the change of level observed in the auxiliary vessel during the interval of the experiment to the equivalent quantity for the primary vessel—

$$\left(\frac{2}{a}+\frac{1}{\mathrm{H}}\right)\delta x=\left(\frac{2}{a}+\frac{1}{\mathrm{H}_{,}}\right)\delta x_{,}.$$

II. To deduce from the corrected change of level in the primary vessel the relative density of ozone and oxygen—

$$\frac{e-1}{e}=m\left(\frac{2}{a}+\frac{1}{\mathrm{H}}\right)\delta x_{,,}.$$

In these formulæ

a is the barometric pressure in terms of the sulphuric acid in the U-tubes.

H, the length of a tube of the same diameter as the U-tube of the primary vessel, and whose capacity is equal to that of the same vessel measured to the mean level of the acid in the U-tube.

$\mathrm{H}_{,}$ the same quantity for the auxiliary vessel.

$\delta x_{,}$ one-half of the change in the difference of levels in the U-tube of auxiliary vessel.

δx, the corresponding quantity for the primary vessel.

$\delta x_{,,}$ half the observed change in the primary vessel corrected by the quantity δx.

m, the ratio of the weights of oxygen and ozone in the gaseous mixture.

e, the relative density of ozone and oxygen.

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THE CHEMICAL GAZETTE.

No. CCCLVII.—September 1, 1857.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Theory of Alkaline Saponification and the Formation of Æthers. *By* J. Bouis.

Some chemists suppose that when fatty bodies are saponified by a small quantity of alkali, a combination of this alkali with the fatty matter takes place without elimination of glycerine,—hence the theory of stearoglycerates, &c. based on the following experiment.

To an ætherial solution of stearine alcohol is added, and afterwards potash until a precipitate is formed; on being heated, the liquid becomes clear, and when it is decomposed by a mineral acid, stearine separates. The author explains this reaction as follows.

When the experiment is repeated, it is easy to see that as soon as the potash is in contact with the dissolved fatty matter, saponification and formation of stearic æther take place; the æther and stearate of potash hold the stearine in solution, and when the alkali is saturated by a mineral acid, the stearine separates, carrying with it the stearic acid and æther formed. This is indicated by the low melting-point of the mixture.

From various experiments, it appears that whenever fatty matters are saponified by a smaller quantity of an alcoholic solution of potash than is necessary for their complete saponification, æthers of fatty acids are formed, at the same time that glycerine separates.

To demonstrate the formation of æthers or free fatty acids, the author saponifies the neutral matter with a standard alcoholic solution of potash; then saturates the alkali exactly by sulphuric acid; separates the products which float upon the water, and washes them completely. The aqueous solution, evaporated to dryness *in vacuo* or on the water-bath, is treated with alcohol, which removes the glycerine and leaves the neutral sulphate of potash. The solid matters left on the filter and dried, are dissolved in æther and treated with lime; by exhausting the dried residue with cold alcohol, the fatty æther is separated; hot sulphuric æther removes the neutral non-saponified matter, and the lime retains the acids which had been set free. The almost instantaneous formation of the æthers under the influence of alkalies is very curious. The interpretation of these phænomena is readily deduced from the constitution of the neutral fatty bodies.

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The saponification of fatty matters by an alcoholic solution of potash is very rapid and convenient, as indicated by Pelouze; but care must be taken to add an excess of alkali, and to expel the alcohol before adding the mineral acid, as otherwise there is risk of the formation of æthers, which, when mixed with the fatty acids, lower their melting-point.

Pelouze has drawn attention to a process made known by M. de Milly. This consists in making use only of a fourth or a fifth of the quantity of lime usually employed. The author indicates the different phases of the operation, and the view which he takes of the acidification.

In treating pure stearine with a small quantity of alkali, monostearine, or distearine must be formed, with a neutral salt, as indicated by the equations,—

$$\underbrace{C^{114}H^{110}O^{12}}_{\text{Tristearine.}} + CaO + HO = \underbrace{C^{78}H^{76}O^{10}}_{\text{Distearine.}} + \underbrace{C^{36}H^{35}O^{3}, CaO}_{\text{Stearate of lime.}}.$$

$$C^{114}H^{110}O^{12} + 2CaO + 2HO = \underbrace{C^{42}H^{42}O^{8}}_{\text{Monostearine.}} + 2(C^{36}H^{35}O^{3}, CaO).$$

The author has always obtained glycerine and unaltered tristearine. The operation, however, is easily understood by supposing, with Wurtz, that glycerine is derived from 3 molecules of water, in which the hydrocarbon, $C^{6}H^{5}$, occupies the place of 3 molecules of hydrogen; thus,—

$$\underset{\text{Water.}}{\left.\begin{matrix}H^{3}\\H^{3}\end{matrix}\right\}O^{6}}, \qquad \underset{\text{Glycerine.}}{\left.\begin{matrix}C^{6}H^{5}\\H^{3}\end{matrix}\right\}O^{6}}.$$

In this case tristearine, or natural stearine, would be

$$\left.\begin{matrix}3(C^{36}H^{35}O^{2})\\C^{6}H^{5}\end{matrix}\right\}O^{6};$$

and by treating it suitably with 3, 2, or 1 equivs. of hydrated base, we shall give rise to neutral stearate alone, or to neutral stearate and acid by the substitution for the hydrocarbon, $C^{6}H^{5}$, of 3 molecules of hydrogen or of metal. Thus,—

$$\left.\begin{matrix}C^{36}H^{35}O^{2}\\C^{36}H^{35}O^{2}(C^{6}H^{5})\\C^{36}H^{35}O^{2}\end{matrix}\right|\left.\begin{matrix}O^{2}\\O^{2}\\O^{2}\end{matrix}\right\}+\left\{\begin{matrix}HM\\HM\\HM\end{matrix}\right|\left.\begin{matrix}O^{2}\\O^{2}\\O^{2}\end{matrix}\right\}=\left\{\begin{matrix}C^{36}H^{35}O^{2}\\C^{36}H^{35}O^{2}\,{}^{M}_{M}\\C^{36}H^{35}O^{2}\,{}^{M}_{M}\end{matrix}\right|\left.\begin{matrix}O^{2}\\O^{2}\\O^{2}\end{matrix}\right\}+\left\{\begin{matrix}C^{6}H^{5}\\H^{3}\end{matrix}\right\}O^{6}.$$

$$\left.\begin{matrix}C^{36}H^{35}O^{2}\\C^{36}H^{35}O^{2}(C^{6}H^{5})\\C^{36}H^{35}O^{2}\end{matrix}\right|\left.\begin{matrix}O^{2}\\O^{2}\\O^{2}\end{matrix}\right\}+\left\{\begin{matrix}HH\\HM\\HH\end{matrix}\right|\left.\begin{matrix}O^{2}\\O^{2}\\O^{2}\end{matrix}\right\}=\left\{\begin{matrix}C^{36}H^{35}O^{2}\\C^{36}H^{35}O^{2}\,{}^{H}_{M}\\C^{36}H^{35}O^{2}\,{}^{M}_{H}\end{matrix}\right|\left.\begin{matrix}O^{2}\\O^{2}\\O^{2}\end{matrix}\right\}+\left\{\begin{matrix}C^{6}H^{5}\\H^{3}\end{matrix}\right\}O^{6}.$$

This mode of representing stearine explains how acidification may be produced with a single equivalent of base; it also furnishes the key to the formation of æthers, alluded to above.

Thus by treating stearine with 2 equivs. of potash in alcohol, 2 equivs. of stearate of potash and 1 equiv. of stearic æther will be formed:—

$$\left.\begin{matrix}C^{36}H^{35}O^{2}\\C^{36}H^{35}O^{2}(C^{6}H^{5})\\C^{36}H^{35}O^{2}\end{matrix}\right|\left.\begin{matrix}O^{2}\\O^{2}\\O^{2}\end{matrix}\right\}+\left\{\begin{matrix}KH\\KH\\(C^{4}H^{5})H\end{matrix}\right|\left.\begin{matrix}O^{2}\\O^{2}\\O^{2}\end{matrix}\right\}=\left\{\begin{matrix}C^{36}H^{35}O^{2}K\\C^{36}H^{35}O^{2}K\\C^{36}H^{35}O^{2}(C^{4}H^{5})\end{matrix}\right|\left.\begin{matrix}O^{2}\\O^{2}\\O^{2}\end{matrix}\right\}+\left\{\begin{matrix}C^{6}H^{5}\\H^{3}\end{matrix}\right\}O^{6}.$$

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Neutral fatty matter being considered as formed of 3 equivs. of acid to 1 equiv. of glycerine, by substituting for the latter 1 equiv. of base, a neutral salt will be formed, and in consequence of this molecular derangement, the smallest cause will suffice to fix water and set free the other 2 equivs. of acid; for

$$\underbrace{C^{114}H^{110}O^{12}}_{\text{Tristearine.}} = 3\underbrace{(C^{36}H^{36}O^{4})}_{\text{Stearic acid.}} + \underbrace{C^{6}H^{8}O^{6}}_{\text{Glycerine.}} - 6HO\text{; therefore}$$

$$C^{114}H^{110}O^{12} + CaO + 5HO = C^{36}\left\{\begin{matrix}H^{35}\\Ca\end{matrix}\right\}O^{4} + 2(C^{36}H^{36}O^{4}) + C^{6}H^{8}O^{6}.$$

Comptes Rendus, July 6, 1857, p. 35.

On the Blood of the Cephalopoda. *By* J. SCHLOSSBERGER.

By the investigation of the evaporated residue of the blood of invertebrated animals, the author has discovered the remarkable fact, that the alkaline phosphates and potash compounds in general are almost entirely wanting in its ashes. As the blood of invertebrate animals is deficient in cells and iron, and in the Vertebrata the organized elements of the blood are the principal seat of those materials, the above facts appear to be explicable from the nature of the blood itself. The specimens of blood which served for these investigations were received by the author from Professor H. Müller of Würzburg.

He obtained the solid residue produced by evaporation in the sun from

I. 2 cub. centim.
II. 1·8 „ „
III. 3·0 „ „
IV. 4·6 „ „

} of the blood of *Sepia*,

of which the three first specimens were derived from different individuals.

The fresh blood of *Octopus*, according to Müller, is translucent, gray, with a bluish tinge; on standing it deposits flakes, consisting principally of the blood-corpuscles, which, however, are on the whole sparingly present. It afterwards becomes more thickly fluid and turbid, and acquires a film, but exhibits no true clot-formation. On the other hand, it crystallizes strongly when evaporated. By heat or alcohol, a very considerable white coagulum is formed; this does not easily dissolve in potash. Acetic acid produces a similar coagulum, which does not disappear in an excess of the acid.

The author determined the amount of solid parts by pouring distilled water over several of the residues in graduted tubes until the original volume of the blood was restored. By comparison of the weights of the fluid blood thus reproduced, and of the solid residue dried at 248° F., he obtained—

from *a.* *Sepia*-blood, 20 per cent. dry substance,
„ *b.* *Sepia*-blood, 18 per cent. „ „
„ *Octopus*-blood, 12·6 per cent. „ „

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consequently considerable differences for the blood of very nearly allied animals. The residues obtained are very similar in appearance. When moistened with water, they swell up without dissolving, and exhibit a slightly alkaline reaction; the water dissolves a considerable quantity of chloride of sodium, but scarcely any organic substance. When poured over with strong acetic acid, the individual laminæ of the residues swelled up strongly, and in the course of a few hours the whole mass had become converted into a perfectly colourless, transparent jelly. It was only after boiling for an hour with fresh acid that the jelly was completely dissolved so as to be capable of filtration. The colourless solution gave yellow flakes with ferrocyanide of potassium; with solution of sulphate of magnesia it gave a whitish turbidity. Tartaric acid did not change it; bichloride of platinum produced a yellow, flocculent precipitate, and infusion of galls a strong gray one. Oxalate of ammonia, when neutralized with ammonia, produced a white precipitate, which did not entirely dissolve in an excess of acetic acid. Sesquichloride of iron gave no precipitate. The solution in acetic acid, when dried, gave a brittle, translucent matter, which was again of a bluish colour, and which, by deflagration with nitrate of potash, showed some SO^3 and PO^5. The residues were insoluble in solution of nitrate of potash, and did not even swell up in it.

In solution of potash the laminæ swelled up, and their bluish colour changed to dark brownish red; in other respects the substance behaves like other proteine bodies with potash. The residues only contained traces of fat. The ashes were first extracted with water; the residuary coal was then burnt away, and the final residue dissolved in muriatic acid, in which it dissolved completely and without effervescence. This residue contained traces of copper, and consisted essentially of phosphates of lime and magnesia, in the extremely small quantities stated below. In both kinds of blood the entire quantity of ash and the proportions of its soluble and insoluble constituents agreed so completely, that in this respect they may be regarded as identical.

Sepia-blood dried at 248° F.				*Octopus*-blood dried at 248° F.			
gave	17·81 per cent. of ash,			17·66 per cent. of ash,			
of which	15·51 „	soluble	salts.	15·40 „	soluble	salts.	
	2·30 „	insoluble		2·26 „	insoluble		

Calculated for the whole of the blood, this gives the following composition for the two kinds of blood:—

Sepia-blood.			*Octopus*-blood.		
Water.....	80		Water.....	87·4	
Organic matters	16·44		Organic matters	10·4	
Mineral matters	3·56	soluble 3·10	Mineral matters	2·2	soluble 1·9
		insoluble 0·46			insoluble 0·3

Liebig's *Annalen*, cii. p. 86.

On Methionic Acid. *By* A. Strecker.

Methionic acid is obtained by passing anhydrous sulphuric acid into refrigerated anhydrous æther, and boiling the compound

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formed with water. It is formed in but small quantity. By saturation with carbonate of baryta methionate of baryta is obtained from the aqueous fluid, forming thin, shining laminæ, which are rhombic tables.

When a flask filled with anhydrous sulphuric acid is reversed over a cylinder containing some æther, so that the two substances come in contact with each other in the form of vapour, methionic acid is also produced; by this means rather more is obtained than in the former way. As soon as the anhydrous sulphuric acid has disappeared, the acid is found in the fluid in the cylinder, partly in the upper ætherial stratum (solution of sulphuric æther), but principally in the stratum of aqueous fluid lying under this. The author has prepared and analysed the following salts of methionic acid.

Methionate of Baryta, $2BaO + C^2 H^2 S^4 O^{10} + 4HO$, crystallized. The 4 equivs. of water disappear at 284° F. When more strongly heated it is decomposed, and sulphur is given off. When fused with hydrate of potash, it furnishes nearly equal equivalents of sulphite and sulphate. Analysis of the dry salt:—

C	3·4	2=	12	3·85
H	0·7	2	2	0·64
S	—	4	64	20·58
O	—	10	80	25·73
BaO	49·1	2	153	49·20

Methionate of Lead, $2PbO, C^2 H^2 S^4 O^{10} + 4HO$, is obtained by saturating carbonate of lead with the aqueous solution of methionic acid, prepared by precipitating the baryta from a solution of methionate of baryta, by sulphuric acid. This salt loses its 4 equivs. of water even at 212° F. It contains 8·6 per cent. of water (calculated 8·4) and 58·5 per cent. oxide of lead (calculated 58·5).

Basic Methionate of Lead, $3PbO, C^2 H^2 S^4 O^9 + HO$, is produced when the solution of the preceding salt is boiled with oxide of lead. It contains 69·2 per cent. oxide of lead (calculated 68 per cent.).

Methionate of Copper, $2CuO, C^2 H^2 S^4 O^{10} + 10HO$, prepared by decomposing the baryta salt with sulphate of copper, crystallizes in blue, rhombic prisms which effloresce. It is easily soluble in aqueous, but insoluble in absolute alcohol. It loses all its water =26·2 per cent. at 212° F., and contains 33·6 per cent. of oxide of copper (calculated 27·5 water and 33·4 oxide of copper).

Methionate of Silver, $2AgO, C^2 H^2 S^4 O^{10}$, is obtained by precipitating the copper from the solution of the copper salt by sulphuretted hydrogen and boiling the fluid with oxide of silver. It forms thin, colourless laminæ, and acquires some colour when exposed to light in a moist state. It contains 55·3 per cent. of silver (calculated 54·4), and loses nothing in weight at 248° F.

Methionate of Potash is an anhydrous salt, crystallizing in long needles.

Methionate of Ammonia crystallizes readily in colourless needles, which undergo no alteration at 284° F.

Methionate of Lime crystallizes in fine silky needles; it is readily soluble in water.

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Methionic Acid may be separated from the lead salt by sulphuretted hydrogen, and obtained by the evaporation of the filtered solution upon the water-bath as a colourless, syrupous fluid, which by long standing over sulphuric acid solidifies into long acicular crystals. These deliquesce in the air, and have a very acid taste. The acid immediately throws down methionate of baryta in crystalline spangles from chloride of barium.

As regards its constitution, methionic acid may be brought into connexion with æthylodithionic acid. If the latter be regarded as a conjugate compound of hyposulphuric acid with æthyle, $C^4 H^5$, $S^2 O^5$, HO, methionic acid may be considered as $C^2 H^2$, $2S^2 O^5$, 2HO, and these formulæ become still more similar when the former is doubled. If the formula of æthylodithionic acid be

$$\left.\begin{matrix} C^4 H^5, S^2 O^4 \\ H \end{matrix}\right\} O^2,$$

methionic acid may be represented by the expression

$$\left.\begin{matrix} C^2 H^2, S^4 O^8 \\ H^2 \end{matrix}\right\} O^4.$$

According to this it would contain $2(S^2 O^4)$ in conjugate combination with the radical $C^2 H^2$, which may displace 2 equivs. of hydrogen.

The author adds, that the methylotetrasulphuric acid of Buckton and Hofmann is nothing but methionic acid.—Liebig's *Annulen*, c. p. 199.

On the Crystalline Body of the Eye.
By MM. Valenciennes *and* Fremy.

The crystalline body of the eye in the Mammalia is formed of fibres which are insoluble in water, and which are united in the centre by an albuminous matter. This albuminous substance coagulates at 149° F., and becomes transparent and amber-yellow by the prolonged action of alcohol. Towards the periphery these fibres are held together by another albuminous substance, which the authors call metalbumen; this does not coagulate under the above-mentioned conditions, and is not rendered blue by treatment with muriatic acid.

As these two substances are anatomically different, forming two distinct parts of the crystalline body, the authors give them particular names. The central part is called *endophacine*; the outer part *exophacine*.

The crystalline body of the eye in Birds, Reptiles, and Batrachia differs but slightly from that of the Mammalia.

The crystalline body of the eye in Fishes is also composed of two different parts. The outer part, the exophacine, also consists of metalbumen; and the central part of a solid albuminous substance insoluble in water, which the authors call *phaconine*.

Even the fibres of the crystalline body in Mammalia, which are held together by albumen or metalbumen to form the endophacine

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and exophacine, have the greatest resemblance to phaconine in their behaviour.

In cataractic crystalline lenses from horses, the substance undergoes a change, resembling that produced by alcohol or boiling water. The albumen and metalbumen of cataractic lenses is, in fact, insoluble in water, and composed of membranes which are somewhat opake, and can be easily separated from each other.

Cataract is not caused by deposition of phosphate of lime, as has been supposed, for the parts affected by cataract leave no more ashes than the sound parts.

The authors state that they received from Boussingault some round bodies which had been found in gold washing in the mine of Antikoia; these were the central nuclei of the lenses of Fishes, and consisted of phaconine.—*Comptes Rendus*, xliv. p. 1122.

On the Compounds of Tantalic Acid with Soda. By H. Rose.

The compounds of tantalic acid with soda are of far greater interest than those with potash and other bases, especially because neutral tantalate of soda may be obtained crystallized, and consequently pure. From its composition we obtain the best notions of the true atomic composition of tantalic acid and the tantalates; and moreover, by the decomposition of tantalate of soda with other neutral salts, the neutral compounds of tantalic acid with other bases may be obtained in the purest state.

The behaviour of tantalic acid towards soda is very different from that towards potash. Whilst tantalate of potash is soluble in all proportions in solutions of hydrate and carbonate of potash, tantalate of soda is perfectly insoluble in solutions of hydrate and carbonate of soda, when these are not too much diluted. In consequence of this property neutral tantalate of soda may be obtained in a state of purity in which neutral tantalate of potash cannot be prepared

When calcined tantalic acid or even hydrated tantalic acid is put into fusing hydrate of soda, a very vivid incandescence takes place; but only if the hydrate of soda had been previously heated to redness. The fused mass, even during the fusion, is not a clear fluid, like the solution of tantalic acid in fusing hydrate of potash, because the tantalate of soda formed is insoluble in hydrate of soda, even in the dry way.

If the fused mass be treated with water, the excess of hydrate of soda is dissolved, and neutral tantalate of soda remains undissolved; this only begins to dissolve when the solution of free alkali has been poured off and replaced by pure water. To obtain the neutral salt pure, the clear solution of the free alkali formed when water is poured over the fused mass, must be drawn off with a siphon, and the undissolved residue treated with hot water, in which it is perfectly soluble. The filtered solution need only be slightly evaporated. On cooling, the neutral salt crystallizes, although never in large crystals. In order that the salt may separate per-

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fectly pure and crystallized, there must be an excess of alkali, although a very small one.

The salt is very difficultly soluble; the solution renders reddened litmus-paper blue. It is less decomposed by boiling than that of tantalate of potash. The composition of the salt is $NaO+2TaO^2$, but it also contains water of crystallization, the amount of which it is difficult to determine by direct experiment. When the crystallized salt is heated only to 212° F., or even below this temperature, it begins to be converted into an insoluble acid tantalate of soda and hydrate of soda, of which the latter takes up carbonic acid, when this is presented to it during its heating. If the dried salt be calcined first by itself and then repeatedly with the addition of small quantities of carbonate of ammonia, the weight sometimes increases and sometimes diminishes, according to the temperature employed in calcination, because by a very strong heat carbonic acid is expelled from the carbonate of soda formed by the acid tantalate of soda. This decomposition of the crystallized neutral salt is interesting. It is not, however, an isolated fact, for the compounds of similar metallic acids, such as antimonic acid, with alkalies, exhibit a similar comportment. It is explained by the author, in accordance with the views as to the nature of water which he has put forward in a long series of memoirs, in the following way:—the water of the salt combines as an acid with 1 part of alkali even at a moderate heat, by which means an acid alkaline tantalate is produced.

The amount of water in the neutral salt is between 7 and 8 atoms; in exact accordance with the results obtained, the amount of water is $7\frac{1}{2}$ atoms. The author decides in favour of 7 atoms of water of crystallization in the salt.

If the tantalate be prepared by fusing tantalic acid with hydrate of soda, treating the mass obtained with water, separating the solution of hydrate of soda from the undissolved residue, dissolving the latter in water, precipitating the tantalate of soda from its solution by solution of hydrate of soda, and washing it either with alcohol or water, a salt is always obtained which contains a small excess of soda, and rather less water of crystallization.

If the solution of the neutral salt be evaporated at a gentle heat, a pasty mass is at last obtained, which when washed with cold water and dried, does not again dissolve in water. If this compound be calcined, also with an addition of carbonate of ammonia, no trace of carbonate of soda can be extracted from the calcined salt by water. The compound is an acid tantalate of soda of the composition $NaO+3TaO^2$; when dried at 212° F., it contains rather more than 2 atoms of water. If this salt, after calcination, be heated with muriate of ammonia and then treated with water, a very acid tantalate of soda of the composition $NaO+9TaO^2$ is obtained.

If the solution of tantalate of soda be mixed with about an equal volume of ordinary alcohol, some soda is extracted from it, and a compound of the formula $2NaO+5TaO^2$ is obtained. When this is decomposed by a great quantity of cold water, and left in contact

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therewith for a long time, an insoluble residue at last separates, consisting of pure tantalic acid, which is remarkable. The dissolved portion, treated with more water, lets fall the entire quantity of dissolved tantalic acid as $2NaO+5TaO^2$, and finally the fluid contains nothing but tantalic acid.

Other weak acids act upon the solution of neutral tantalate of soda in the same way as water. As, however, almost every acid is stronger than water when this plays the part of an acid, the decomposition of the tantalate goes further with acids than with water, and if an acid of a tolerable strong nature be employed, the decomposition is complete.

When carbonic acid gas is conducted through a solution of neutral tantalate of sada, the compound $NaO+9TaO^2$ is precipitated. When a current of sulphuretted hydrogen is passed through it, the compound $NaO+12TaO^2$ is thrown down. The neutral salt therefore loses $\frac{1}{3}$rd of its soda by water, $\frac{7}{9}$ths by carbonic acid, and $\frac{8}{9}$ths by sulphuretted hydrogen. When a still stronger acid, such as sulphurous acid, is employed, pure hydrated tantalic acid is separated from the solution of neutral tantalate of soda. But if the acid employed be a very strong one, not only is all the soda abstracted from the tantalic acid, but the latter even becomes basic towards the strong acid. Sulphuric acid, for example, throws down tantalic acid from the solutions of its alkaline salts as sulphate of tantalic acid. Other acids, such as muriatic and nitric acids, certainly abstract the entire amount of base from the tantalic acid, and unite as acids with the tantalic acid, but form therewith soluble compounds. Even sulphuric acid may furnish similar soluble compounds with tantalic acid, but these are thrown down when the solution is heated.

The behaviour of carbonate of soda with tantalic acid is different from that of hydrate of soda. From the mass obtained by fusing them together, water dissolves the excess of carbonate of soda, in which tantalate of soda is completely insoluble. The residue, treated with hot water, leaves a compound undissolved, the composition of which may be expressed by $2NaO+5TaO^2$; whilst on the evaporation of the washing-water at a gentle heat, crusts are deposited on the walls of the capsule, and these singularly possess the same composition. By very long-continued washing, however, more soda may constantly be extracted from the acid tantalate, and at last the compound $NaO+5TaO^2$, or rather $2NaO+9TaO^2$, is obtained.

If weighed quantities of carbonate of soda and tantalic acid be fused together, and the amount of carbonic acid expelled be determined by the loss of weight, different results are obtained according as a weaker or stronger heat has been allowed to act for a shorter or longer time. The author has varied the degree of heat in these experiments in many ways, and the detailed results of his researches are given in his memoir. If the fusion be effected by means of charcoal fire, the compound $NaO+TaO^2$ is produced. If the fusion be longer continued, so that complete solution takes place, the compound $3NaO+2TaO^2$ is formed, but this becomes still more basic by longer fusion, and acquires the composition $15NaO+8TaO^2$,

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which, if the fusion had been continued, would undoubtedly have passed to $2NaO + TaO^2$.—*Bericht der Akad. der Wiss. zu Berlin*, 1857, p. 282.

On Inverse Substitutions. *By* M. BERTHELOT.

1. In his previous memoir the author stated that bromide of æthylene, $C^4 H^4 Br^2$, heated to 527° F. with copper, water, and iodide of potassium, principally regenerates the olefiant gas, $C^4 H^4$, which formed it; when heated with water and iodide of potassium, it produces especially hydruret of æthyle, $C^4 H^6$, a compound in which the bromine of the bromide of æthylene is replaced by hydrogen, so that hydrogen is added to the olefiant gas. All these reactions are more distinct the more slowly the operation is performed, and the nearer the temperature is kept to 527° F.

Bromide of propylene, $C^6 H^6 Br^2$, presents analogous reactions. Heated to 527° F. with copper, water, and iodide of potassium, it principally regenerated propylene, $C^6 H^6$; with water and iodide of potassium, it produces especially hydruret of propyle, $C^6 H^8$, in which the bromine is replaced by hydrogen.

Bromide of butylene, $C^8 H^8 Br^2$, and bromide of amylene, $C^{10} H^{10} Br^2$, treated in the same way (with copper), also reproduced butylene, $C^8 H^8$, and amylene, $C^{10} H^{10}$. By this means the alcoholic hydrocarbons, æthylene, propylene, butylene, and amylene, contained in a gaseous mixture, may be separated from each other in the form of bromides, and then regenerated in the gaseous form which they originally possessed.

2. The author has endeavoured to extend the same methods to other compounds, as chloride of æthylene, chloroform, bromoform, iodoform, perchloride of carbon, bromide of brominated propylene, and trichlorhydrine.

Chloride of æthylene, $C^4 H^4 Cl^2$, is much more difficult to decompose completely than bromide of æthylene. When treated as above, either with or without copper, a certain quantity of olefiant gas is, however, regenerated; but this gas is mixed with monochlorinated æthylene, $C^4 H^3 Cl$.

Chloroform, $C^2 H Cl^3$, bromoform, $C^2 H Br^3$, and iodoform, $C^2 H I^3$, when decomposed either by zinc alone, by copper, water, and iodide of potassium, or by water and iodide of potassium only, produce a mixture of marsh-gas, $C^2 H^4$, hydrogen, and in the two latter cases, oxide of carbon and carbonic acid. At the same time, a small quantity of a gaseous or very volatile compound is formed; this is absorbable by bromine, but its nature and origin could not be determined with certainty.

Perchloride of carbon, $C^2 Cl^4$, heated with iodide of potassium, copper, and water, produced a mixture of marsh-gas, oxide of carbon, hydrogen, and carbonic acid.

Bromide of brominated propylene, $C^6 H^5 Br^3$, treated in the same way, produced a mixture of propylene, $C^6 H^6$, hydruret of propyle, $C^6 H^8$, and carbonic acid, so that the 3 equivs. of bromine contained in this compound may be replaced by 3 equivs. of hydrogen.

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Trichlorhydrine, $C^6 H^5 Cl^3$, one of the hydrochloric æthers of glycerine, isomeric with chloride of chlorinated propylene, when treated as above, produced propylene, $C^6 H^6$, hydruret of propyle, $C^6 H^8$, hydrogen, and carbonic acid. Thus we may pass by a new way from glycerine, $C^6 H^8 O^6$, to the corresponding hydrocarbons, and especially get rid of all the oxygen which it contains; it is sufficient to eliminate all this oxygen in the form of water, replacing this water by muriatic acid,—

$$C^6 H^8 O^6 - 6HO + 3HCl = C^6 H^5 Cl^3.$$

Hydrogen is then substituted for the chlorine.—*Comptes Rendus*, June 29, 1857, p. 1359.

Note on some New Compounds of Silicium.
By MM. Wöhler *and* Buff.

In continuing the researches upon new compounds of silicium which M. Dumas has communicated to the Academy, we have found that the gas which is disengaged from the positive pole when an electric current is passed through a solution of chloride of sodium, employing as electrodes siliciferous aluminium and siliciuret of hydrogen, inflames in contact with the air, and burns with a dazzling white flame, producing a white siliceous smoke. If a capsule of porcelain be interposed in the flame, brown spots of amorphous silicium are obtained upon it. On passing it through an incandescent glass tube, a deposition of a brown speculum of amorphous silicium takes place. It also inflames when mixed with gaseous chlorine. We are still unable to explain the formation of this body, which is paradoxical, inasmuch as it occurs at the positive pole, whilst there is an evolution of hydrogen at the negative pole. Nor have we yet succeeded in determining its quantitative composition as it is always mixed with variable quantities of free hydrogen. From our experiments, however, it seems to contain an equal volume of hydrogen.

We have found, also, that siliciuret of hydrogen is formed when aluminium, containing as usual silicium only, is dissolved in muriatic acid; in this case it is always mixed with such an excess of free hydrogen, that it does not inflame by contact with the air.

The experiments that we have undertaken to determine the composition of the new oxide and chloride, have not as yet given satisfactory results. Most of the numbers obtained certainly accord with the formulæ $Si^2 O^5$ and $Si^2 Cl^5$; but this composition does not appear probable, and we are not sure that we have not hitherto had to do with mixtures.

It is, however, certain that the white oxide obtained by the decomposition of the chloride with water, is a hydrate which does not lose its water at 572° F. When heated to redness, it takes fire and evolves hydrogen which inflames. When the new chloride is passed through an incandescent tube, it is decomposed into chloride, $SiCl^3$, and a brown speculum of amorphous silicium.

We have since prepared the corresponding bromide and iodide.

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They are obtained by heating silicium to a dull red heat in a current of hydrobromic or hydriodic acid gas. The bromide is a very volatile fuming liquid; the iodide is a solid body of a deep-red colour, very fusible and volatile; under the influence of moist air, it evolves hydriodic acid, and becomes converted into white oxide.—*Comptes Rendus*, June 29, 1857, p. 1344.

On a New Base from the Juice of Flesh. By A. STRECKER.

The syrupous mother-liquor which is obtained in the preparation of creatine as described by Liebig, contains a crystallizable body with weak basic properties, to which the author gives the provisional name of sarcine. It is obtained by precipitation with metallic salts, of which acetate of copper is the best; the precipitate is washed with boiling water and decomposed by sulphuretted hydrogen. The sarcine deposited when the filtrate is concentrated is purified by being dissolved in boiling water, adding hydrated oxide of lead, filtering and precipitating the lead by sulphuretted hydrogen.

On the cooling of the saturated aqueous solution, sarcine separates slowly in the form of a white, indistinctly crystalline powder, which often covers the wall of the vessel with a coherent, dense coating. It remains unaltered when heated to 302° F. or higher. When more strongly heated, it evolves hydrocyanic acid without fusing, and furnishes a white, hardly volatile sublimate (cyanuric acid?), leaving a carbonaceous residue. It dissolves in 300 parts of cold and in 78 parts of boiling water; of boiling alcohol it requires 900 parts for solution. The solutions do not render reddened litmus-paper blue. In muriatic acid, potash, ammonia, and even baryta-water sarcine dissolves more readily than in water, sometimes in great abundance. Concentrated sulphuric or nitric acid also dissolves it in considerable quantity, without the least coloration or evolution of gas. The analysis of air-dried sarcine led to the formula $C^{10} H^4 N^4 O^2$.

With muriatic acid sarcine furnishes a salt which crystallizes in colourless nacreous tables of the formula $C^{10} H^4 N^4 O^2$, $HCl + 2HO$, and forms with perchloride of platinum a yellow crystalline compound, $C^{10} H^4 N^4 O^2$, $HCl + PtCl^2$. Nitrate of sarcine forms limpid crystals, which become opake in the air. Sulphate of sarcine crystallizes (from alcohol) in colourless needles.

Sarcine also furnishes compounds with bases. It dissolves in solution of potash and is precipitated therefrom by carbonic acid. From a solution in boiling baryta-water, the addition of a cold saturated solution of hydrate of baryta causes the separation of colourless acicular crystals of the composition $C^{10} H^4 N^4 O^2 + 2BaO + 2HO$. The compounds with oxide of zinc, oxide of copper, and oxide of mercury are insoluble in water. With nitrate of silver sarcine forms a flocculent precipitate, which dissolves in hot nitric acid, and has the formula $C^{10} H^4 N^4 O^2 + AgO, NO^5$. In an ammoniacal solution of silver, the addition of solution of sarcine causes a precipitate of the composition $C^{10} H^4 N^4 O^2$, $2AgO$.

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Sarcine has the same per-centage composition as Scheerer's hypoxanthine, $C^5 H^2 N^2 O$, which it also resembles in some properties. The author, however, does not regard the two bodies as identical.

A solution of urate of potash mixed with muriate of sarcine furnishes a precipitate of urate of sarcine, $C^{10} H^4 N^4 O^2 + C^{10} H^4 N^4 O^6$, which agrees in its composition with xanthine. A comparison of the two bodies, however, proved them to be distinct.

The quantity of sarcine contained in beef is stated by the author at 0·22 part in 1000 parts of flesh.

As sarcine is very stable, it appears probable that it may be separated unaltered in the urine. A very similar body is actually found in human urine, but the author will not positively state that this is sarcine.—Liebig's *Annalen*, cii. p. 204.

PROCEEDINGS OF SOCIETIES.

Royal Society.

June 15, 1857. (The Lord Wrottesley, President, in the Chair.)

"Contributions towards the History of the Phosphorus-, Arsenic-, and Antimony-Bases." By A. W. Hofmann, Ph.D., LL.D., F.R.S.

The facility with which the phosphorus-bases can be obtained by the action of zincethyle upon terchloride of phosphorus, has induced me to study the action of this agent upon the terchlorides of arsenic and antimony. I have found that triethylarsine and triethylstibine, hitherto obtainable only with difficulty, by submitting the alloys of potassium with arsenic and antimony to the action of iodide of ethyle, may be procured by this process as readily and as abundantly as the phosphorus-bases.

In attempting to identify the substances obtained by the new process with those prepared by the old one, by the analysis of platinum- and gold-salts, I have been led to the discovery of a series of compounds of remarkable beauty.

Since the study of these bodies, and especially of their derivatives, which are particularly numerous and interesting, will involve considerable time, I beg leave to submit to the Royal Society, before the session closes, a brief sketch of those substances, the composition of which I have already established by analysis.

On adding a solution of bichloride of platinum to an alcoholic solution of triethylphosphine, of triethylarsine or triethylstibine as long as the colour of the platinum solution entirely disappears, the liquid deposits after a few moments magnificent slightly yellow or colourless crystals. The three salts thus formed may be considered as the chlorides of three compound ammoniums containing platinum and ethyle, united respectively with phosphorus, arsenic and antimony. They have the following composition:—

$$\text{Chloride of Platophosphethylium...} \left.\begin{matrix} Pt \\ E \\ E \\ E \end{matrix}\right\} P\,Cl.$$

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$$\text{Chloride of Platarsethylium} \ldots\ldots \left.\begin{matrix}\text{Pt}\\ \text{E}\\ \text{E}\\ \text{E}\end{matrix}\right\} \text{As Cl.}$$

$$\text{Chloride of Platostibethylium} \ldots\ldots \left.\begin{matrix}\text{Pt}\\ \text{E}\\ \text{E}\\ \text{E}\end{matrix}\right\} \text{Sb Cl.}$$

On substituting for the bichloride of platinum a solution of terchloride of gold, perfectly similar phenomena present themselves. The gold solution is entirely decolorized, and the colourless liquids deposit three gold compounds, which, remarkably enough, are of a dazzling white colour and silvery lustre.

Analysis has proved these salts to correspond to the platinum-salts just mentioned, the platinum being replaced by an equivalent quantity of gold.

The formulæ of these substances are—

$$\text{Chloride of Auro-phosphethylium} \ldots \left.\begin{matrix}\text{Au}\\ \text{E}\\ \text{E}\\ \text{E}\end{matrix}\right\} \text{P Cl.}$$

$$\text{Chloride of Auro-arsethylium} \ldots\ldots \left.\begin{matrix}\text{Au}\\ \text{E}\\ \text{E}\\ \text{E}\end{matrix}\right\} \text{As Cl.}$$

$$\text{Chloride of Auro-stibethylium} \ldots\ldots \left.\begin{matrix}\text{Au}\\ \text{E}\\ \text{E}\\ \text{E}\end{matrix}\right\} \text{Sb Cl.}$$

The complementary products formed in these reactions remain in the mother-liquors of the several salts, from which they separate in the form of oily compounds which gradually solidify into crystalline masses. These I have not yet examined.

A glance at the above formulæ shows that the new compounds which form the subject of this note correspond to the chloride of platammonium,

$$\left.\begin{matrix}\text{Pt}\\ \text{H}\\ \text{H}\\ \text{H}\end{matrix}\right\} \text{N Cl.}$$

It remains to be ascertained whether the chloride of plato-diammonium,

$$\left.\begin{matrix}\text{H}\\ \text{H}\\ \text{H}\end{matrix}\right\} \text{N} \left.\begin{matrix}\text{Pt}\\ \text{H}\\ \text{H}\\ \text{H}\end{matrix}\right\} \text{N Cl,}$$

is likewise represented in the phosphorus-, arsenic-, and antimony-series.

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"On a New Series of Compounds derived from Ammonia and its Analogues." By Edward Frankland, Ph.D., F.R.S.

Although zincethyle and its homologues are now well known to be capable of replacing electro-negative elements by ethyle, &c., yet it could scarcely have been anticipated, that substitutions of an almost opposite character would be effected by the same reagent; nevertheless I find that zincethyle is capable of removing one of the atoms of hydrogen in ammonia and its analogues, and of replacing it by zinc, thus forming a series of bodies which strongly remind us of the amide and nitride of potassium. The general nature of this reaction by which the compounds described below are produced, may be thus expressed:—

$$N\left\{\begin{matrix} x \\ y \\ H \end{matrix} + \begin{matrix} Zn \\ C_4H_5 \end{matrix}\right\} = N\left\{\begin{matrix} x \\ y \\ Zn. \end{matrix} + \begin{matrix} C_4H_5 \\ H \end{matrix}\right\}.$$

When dry ammoniacal gas is passed through an ethereal solution of zincethyle, it is rapidly absorbed, and soon afterwards torrents of a combustible gas free from nitrogen begin to be evolved. After the current has been continued for more than an hour, the absorption altogether ceases, and the ethereal liquid deposits a copious white amorphous precipitate, which yielded on analysis numbers leading to the formula

$$N\left\{\begin{matrix} H \\ H \\ Zn. \end{matrix}\right.$$

The analysis of the combustible gas proved that 1 vol. consumed 3·43 vols. oxygen, and generated 1·95 vol. carbonic acid; numbers almost identical with those yielded by hydride of ethyle, with which the gas is also identical in specific gravity. These results prove that zincethyle acts upon ammoniacal gas in the following manner:—

$$N\left\{\begin{matrix} H \\ H \\ H \end{matrix} + \begin{matrix} Zn \\ C_4H_5 \end{matrix}\right\} = N\left\{\begin{matrix} H \\ H \\ Zn \end{matrix} + \begin{matrix} C_4H_5 \\ H \end{matrix}\right\}.$$

The solid product of the reaction, for which I propose the name *zincamide*, is a white amorphous body insoluble in ether, and instantly decomposed by water and alcohol, with evolution of great heat, and in such a manner as to regenerate ammonia. Thus with water the following equation expresses the reaction:—

$$N\left\{\begin{matrix} H \\ H \\ Zn \end{matrix} + \begin{matrix} H \\ H \end{matrix}\right\} O_2 = N\left\{\begin{matrix} H \\ H \\ H \end{matrix} + \begin{matrix} Zn \\ H \end{matrix}\right\} O_2.$$

Heated with iodide of ethyle in a sealed tube at 145° C., zincamide gives iodide of zinc and iodide of diethylammonium—

$$N\left\{\begin{matrix} H \\ H \\ Zn \end{matrix} + 2\begin{matrix} C_4H_5 \\ I \end{matrix}\right\} = N(C_4H_5)_2H_2I + ZnI.$$

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Nitride of Zinc.

Zincamide can bear a temperature of 200° C. without decomposition, but at a low red heat it is decomposed into nitride of zinc and ammonia:—

$$3N\left\{\begin{matrix}H\\H\\Zn\end{matrix}\right. = 2N\left\{\begin{matrix}H\\H\\H\end{matrix}\right. + N\left\{\begin{matrix}Zn\\Zn\\Zn.\end{matrix}\right.$$

Nitride of zinc is a grey pulverulent body, which is neither fused, decomposed, nor volatilized at a red heat out of contact with air. It is decomposed by water with great violence; in fact, if the nitride be merely moistened with water, it becomes red-hot. Several analyses prove that the formula of nitride of zinc is

$$N\left\{\begin{matrix}Zn\\Zn\\Zn.\end{matrix}\right.$$

The study of the products of its decomposition by water shows that the reaction may be thus expressed:—

$$N\left\{\begin{matrix}Zn\\Zn\\Zn\end{matrix}\right. + 6HO = N\left\{\begin{matrix}H\\H\\H\end{matrix}\right. + 3\left\{\begin{matrix}Zn\\H\end{matrix}\right\} O_2.$$

Zincphenylimide.

$$N\left\{\begin{matrix}C_{12}H_5\\H\\Zn.\end{matrix}\right.$$

This body is produced by the action of zincethyle upon anhydrous aniline. The reaction is so violent that it requires to be moderated by diluting the zincethyle with ether. Heat is evolved, and a large quantity of a combustible gas is rapidly generated. At length the liquid becomes a white, semisolid, opake mass. Analysis proved the gas to be pure hydride of ethyle, whilst the solid body regenerated aniline in contact with water. The production of zincphenylimide may therefore be thus expressed:—

$$N\left\{\begin{matrix}C_{12}H_5\\H\\H\end{matrix}\right. + \left\{\begin{matrix}Zn\\C_4H_5\end{matrix}\right\} = N\left\{\begin{matrix}C_{12}H_5\\H\\Zn\end{matrix}\right. + \left\{\begin{matrix}C_4H_5\\H\end{matrix}\right\}.$$

Zincphenylimide is a white amorphous body very similar to zincamide. Like the latter body, it is instantly decomposed by water, aniline being regenerated:—

$$N\left\{\begin{matrix}C_{12}H_5\\H\\Zn\end{matrix}\right. + \left\{\begin{matrix}H\\H\end{matrix}\right\} O_2 = N\left\{\begin{matrix}C_{12}H_5\\H\\H\end{matrix}\right. + \left\{\begin{matrix}Zn\\H\end{matrix}\right\} O_2.$$

Diethylzincamine.

$$N\left\{\begin{matrix}C_4H_5\\C_4H_5\\Zn.\end{matrix}\right.$$

This body is produced by the action of zincethyle upon diethyl-

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amine. The reaction requires to be aided by heat. Pure hydride of ethyle is evolved, and the following equation expresses the reaction :—

$$N\left\{\begin{matrix}C_4H_5\\C_4H_5\\H\end{matrix}+\begin{matrix}Zn\\C_4H_5\end{matrix}\right\}=N\left\{\begin{matrix}C_4H_5\\C_4H_5\\Zn\end{matrix}+\begin{matrix}C_4H_5\\H\end{matrix}\right\}.$$

Its reactions are quite similar to those of the bodies above described.

Zincoximide.

$$N\left\{\begin{matrix}C_2O_2\\H\\Zn.\end{matrix}\right.$$

Dry oxamide and pure zincethyle are without any action upon each other at ordinary temperatures, but the heat of a water-bath is sufficient to establish a violent reaction, torrents of pure hydride of ethyle are evolved, and zincoximide combined with zincethyle remains in the retort. The following equation expresses the reaction :—

$$N\left\{\begin{matrix}C_2O_2\\H\\H\end{matrix}+2(ZnC_4H_5)=N\left\{\begin{matrix}C_2O_2\\H\\Zn\end{matrix}+\begin{matrix}Zn\\C_4H_5\end{matrix}\right\}+\begin{matrix}C_4H_5\\H\end{matrix}\right\}.$$

Zincacetimide.

$$N\left\{\begin{matrix}C_4H_3O_2\\H\\Zn.\end{matrix}\right.$$

Acetamide and zincethyle act upon each other very violently; a large quantity of gas is evolved, which analysis proves to be hydride of ethyle. Zincacetimide is contained in the residue as a white, amorphous, pulverulent solid, which is reconverted into acetamide by contact with water.

These reactions establish the fact, that by the action of zincethyle one of the atoms of hydrogen, in ammonia and analogous nitrogen compounds, combines with ethyle and becomes replaced by zinc. It will be interesting to extend this reaction to the nitryles, especially such as contain electro-negative radicals of the othyle family, since we may thus expect to obtain a new series of double radicals, amongst which the ketones will perhaps find a home. I hope soon to lay the results of this extension of the investigation before the Royal Society.

"Remarks on a New Class of Alcohols." (Second Note.) By A. W. Hofmann, LL.D., F.R.S., and Auguste Cahours, F.C.S.

In a former communication (Proceedings, vol. viii. No. 19), we endeavoured to delineate the characters of a new alcohol—the Allylic alcohol, which is the prototype of a new class of alcohols. We have since continued these researches in order to complete the history of this remarkable compound.

In submitting to the Royal Society the full account of our experiments upon the subject, we beg leave to mention in this abstract briefly some additional compounds which we have examined since our last communication.

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Sulphide of Allyle (Garlic Oil), $C_{12} H_{10} S_2$. — When iodide of allyle is allowed to fall drop by drop into a concentrated alcoholic solution of protosulphide of potassium, a very energetic action ensues, the liquid becomes very hot, and an abundant crystalline deposit takes place of iodide of potassium. It is important that the iodide of allyle should only be added gradually to avoid spirting, by which a part of the product would be lost. As soon as the action ceases, the liquid is mixed with a slight excess of sulphide of potassium; addition of water now separates a light yellowish limpid oil possessing a strong smell of garlic. When rectified, this liquid becomes colourless, it boils at 140° C., and gives with nitrate of silver a crystalline precipitate soluble in a boiling mixture of alcohol and water, and separating from this solvent in the form of beautiful white needles, absolutely identical with those which the natural essence of garlic produces. Sulphide of allyle also comports itself with corrosive sublimate and with bichloride of platinum exactly like the natural garlic oil.

Allyle-Mercaptan, $C_6 H_6 S_2$.—When in the process for the preparation of the preceding compound the protosulphide of potassium is replaced by the hydrosulphate of sulphide of potassium, a volatile product is obtained, having a similar but more ethereal odour. This substance acts with energy upon protoxide of mercury, with which it forms a compound, dissolving in boiling alcohol, and separating from it on cooling in the form of pearly scales of remarkable brilliancy, which present the greatest resemblance to the mercaptide of mercury. The liquid obtained in the above-mentioned reaction boils at 90°, and possesses a composition and an aggregate of properties which closely resemble those of the mercaptan of the ethyle-series, being, in fact, the allylic mercaptan, $C_6 H_6 S_2$.

Allylamine, $C_6 H_7 N$.—By boiling cyanate of allyle ($C_8 H_5 NO_2$) with a concentrated solution of caustic potassa until the oily layer entirely disappears, a complete decomposition ensues, and the residue contains only a mixture of carbonate of potassium with an excess of the alkaline hydrate; the volatile products condensed in hydrochloric acid furnish a saline mass which may be obtained crystalline on evaporation. This substance is always a mixture, the constituents of which vary both in nature and properties. The action of potassa on it not only separates a base, which is readily soluble in water, but also insoluble basic oils, the boiling-point of which rises to 180° C. Simple distillation of the liberated bases appears to give rise to decompositions, and thus to induce further complication. We have not succeeded in ascertaining with perfect precision the nature of this mixture, but we have found that it invariably contains a considerable quantity of a base which bears the same relation to allylic alcohol that is observed between ethylamine and ordinary alcohol. The formation of this substance, which we propose to designate allylamine, $C_6 H_7 N$, is perfectly analogous to the production of ethylamine by means of cyanate of ethyle.

Diallylamine, $C_{12} H_{11} N$.—Impure allylamine, obtained by the action of potassa on the cyanate, when digested with a second quan-

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tity of iodide of allyle is rapidly changed into a mass of hydriodates of new compounds. This crystalline mass evidently contains a considerable quantity of the hydriodate of diallylamine, but to succeed in separating it from this very complicated mixture would have required a more considerable quantity of substance than we had at our disposal.

Triallylamine, $C_{18}\ H_{15}\ N$.—The oxide of tetrallylammonium, to which we shall presently allude, submitted to the action of heat, is decomposed, with liberation of a basic oil. The perfect analogy of the oxide of tetrallylammonium with the corresponding ethyle-compound, leaves no doubt respecting the nature of this basic substance. It is obviously triallylamine. When saturated with hydrochloric acid and mixed with bichloride of platinum, it deposits a yellow platinum-salt, the analysis of which leads to the formula

$$\left.\begin{matrix} C_6\ H_5 \\ C_6\ H_5 \\ C_6\ H_5 \end{matrix}\right\} N,\ H\ Cl,\ Pt\ Cl_2.$$

Oxide of Tetrallylammonium, $C_{24}H_{20}NO,HO$.—The chief product of the action of ammonia upon iodide of allyle is a magnificent crystalline compound, which is deposited from the solution resulting from the reaction. Iodide of allyle is rapidly attacked even by an aqueous solution of ammonia at the common temperature. By a few days' contact a large quantity of the iodide dissolves, and the solution becomes a solid mass. If no deposition of crystals take place from the solution, it is only necessary to add a concentrated solution of caustic potassa, which causes the separation of an oily layer that speedily solidifies. The crystals thus formed are the iodide of tetrallylammonium, which, like the corresponding compound of the ethyle-series, is but slightly soluble in solution of potassa. It is obtained pure by exposing it to the air until the potassa is converted into carbonate, and then recrystallizing it from absolute alcohol.

The iodide, by treatment with oxide of silver, is immediately transformed into the oxide. This forms an alkaline solution, which possesses all the properties of the oxide of tetrethylammonium.

The iodide contains

$$\left.\begin{matrix} C_6\ H_5 \\ C_6\ H_5 \\ C_6\ H_5 \\ C_6\ H_5 \end{matrix}\right\} N\ I.$$

On taking a retrospective glance at the results obtained in this inquiry, it is obvious that propylene, a homologue of olefiant gas, is susceptible of furnishing a mono-acid alcohol, which bears to it the same relation that is observed between methyl-alcohol and marsh-gas, or between benzoic alcohol and toluole, the analogue of marsh-gas among the derivatives of the aromatic acids. The hydrocarbons homologous and analogous to marsh-gas, the homologues of olefiant gas, and indeed probably a very considerable number of other hydrocarbons, may be regarded as starting-points for the production of

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mono-acid alcohols and of all their derivatives. All these alcohols are formed by the fixation of two equivalents of oxygen, which oxidation, however, cannot be effected directly, but is accomplished by a series of substitution-processes.

$$\underbrace{C_2H_4}_{\text{Marsh-gas.}} + O_2 = \underbrace{C_2H_4O_2}_{\text{Methylic alcohol.}},$$

$$\underbrace{C_{14}H_8}_{\text{Toluol.}} + O_2 = \underbrace{C_{14}H_8O_2}_{\text{Benzoylic alcohol.}},$$

$$\underbrace{C_6H_6}_{\text{Propylene.}} + O_2 = \underbrace{C_6H_6O_2}_{\text{Allylic alcohol.}},$$

But olefiant gas and its homologues are capable of furnishing mono-acid alcohols by another reaction, which has not yet been applied to the series of bodies homologous to marsh-gas. In fact, we have learnt by the beautiful researches of M. Berthelot that olefiant gas and its homologues are capable of being transformed into alcohols by the absorption of two equivalents of water; olefiant gas furnishes by this reaction ordinary alcohol, and propylene, propylic alcohol; thus—

$$\underbrace{C_4H_4}_{\text{Olefiant gas.}} + 2HO = \underbrace{C_4H_6O_2}_{\text{Ethylic alcohol.}},$$

$$\underbrace{C_6H_6}_{\text{Propylene.}} + 2HO = \underbrace{C_6H_8O_2}_{\text{Propylic alcohol.}}.$$

Olefiant gas, then, and all its homologues are capable of furnishing *two* mono-acid alcohols, exhibiting slightly different features, but presenting in all their principal characters the most obvious analogy. The alcohols formed by fixation of water, such as ethylic alcohol, have long been well known; in fact, the detailed study which has been made during the last quarter of a century of most of their derivatives, has exercised the most beneficial influence upon the development of organic chemistry.

The same remark does not apply to the alcohols produced from these same hydrocarbons by fixation of oxygen. The history of allylic alcohol, which we have endeavoured to trace in the preceding pages, and to which of late important contributions have been furnished, moreover, by MM. Berthelot and De Luca and by M. Zinin, begins to throw light also upon this second group of alcohols. For this reason the discovery of allylic alcohol appears to claim the attention of chemists, even if it had not assisted in fixing, in the system of organic compounds, the exact position of several very interesting natural products, viz. the sulphuretted oils furnished by the bulbs of the garlic (*Allium sativum*) and the seeds of the black mustard (*Sinapis nigra*), which it had not been possible up to the present time to group around a similar centre.

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THE CHEMICAL GAZETTE.

No. CCCLVIII.—September 15, 1857.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Constitution and True Formula of Oxalic Acid. By A. WURTZ.

OXALIC acid has long been regarded as an oxide of carbon, intermediate between carbonic oxide and carbonic acid; but of late another theory has been set up, according to which oxalic acid is to be regarded as a true bibasic organic acid, containing 4 equivs. of carbon, 2 equivs. of hydrogen, and 8 equivs. of oxygen. Founded chiefly on the property possessed by this acid of forming acid and double salts like tartaric acid, this theory was still destitute of experimental proof. If the molecule of oxalic acid is really so complicated as expressed by the formula $C^4 H^2 O^8$, there is some difficulty in classifying it. What is its mode of formation; from what body is it derived; and what place must it occupy in the classification of organic substances? In the reactions in which oxalic acid is formed, it appears as a fortuitous product of the oxidation of complex organic matters, and its connexion with its primitive body cannot be detected. When acetic acid is formed at the expense of the elements of alcohol, the transformation may be followed step by step. The radical of alcohol is modified by substitution to form that of acetic acid; with the exception of this modification no change takes place in the arrangement of the molecule.

The author states that oxalic acid is derived from glycol, discovered by him by adding hydrogen and oxygen to the elements of olefiant gas. He regards this as a diatomic alcohol*. During oxidation glycol is converted into oxalic acid, just as alcohol is converted into acetic acid.

1. When a few drops of glycol are brought into contact with platinum-black, a very brisk reaction takes place; the platinum-black becomes incandescent, the glycol disappears, and carbonic acid is set free in abundance. This evolution of carbonic acid is also produced when the glycol is diluted with several volumes of water. The mixture becomes heated, and if it be exhausted with water at the close of the reaction, the evaporation of the solution gives only a fixed acid, which forms a soluble salt with lime, and reduces the

* See Chem. Gaz., vol. xiv. p. 361.

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salts of silver. These are the characters of glycolic acid, the oxidation which the glycol undergoes in these circumstances being too strong.

2. About 10 grms. of glycol were dissolved in 4 volumes of weak nitric acid of 1·329 spec. grav.; the solution was left standing for several days at the ordinary temperature. When evaporated *in vacuo* over lime, it left a syrupous and very acid residue. This syrup was mixed with water, and neutralized with chalk. The filtered solution having been mixed and concentrated, was precipitated by alcohol, and furnished an abundant precipitate, which was redissolved in boiling water.

The liquid formed a mass on cooling, depositing a lime-salt, crystallizing in tufts and warts formed by very fine interlaced needles. This was purified by recrystallization. At 248° F. it loses 22 per cent. of water. The dry salt contains—

	Found.			Calculated.
C	24·87	25·00	4	25·26
H	3·52	3·40	3	3·15
O	..	..	5	
CaO	28·93	..	1	29·47

The formula $C^4 H^3 CaO^6$ is that of glycolate of lime. The acid which it contains, $C^4 H^4 O^6$, was first pointed out by Strecker and Socoloff as a product of the oxidation of glycocoll or sugar of gelatine. It is identical or isomeric with the acid obtained by Cloëz from the mother-liquors of fulminate of mercury, which he called *homolactic acid.* It is the homologue of lactic acid, $C^6 H^6 O^6$. It is possible that it affects two modifications like lactic acid itself. The lime-salt which greatly resembles lactate of lime, appears to differ from the ordinary glycolate of lime by its slight solubility in water. It swells up greatly when calcined; and the acid which it contains readily reduces the salts of silver like ordinary glycolic acid.

When the lime is exactly precipitated by oxalic acid, and the solution is evaporated first on the water-bath and afterwards *in vacuo*, crystallized glycolic acid is obtained. The alcoholic liquid from which the glycolate of lime was deposited, contained no substance analogous to aldehyde and capable of forming a crystallizable compound with bisulphite of soda.

3. Three grammes of glycol were boiled for a few minutes with 4 volumes of weak nitric acid. A very brisk reaction occurred, abundant red vapours were evolved, and the liquid left standing till the next day formed a mass of crystals. These were oxalic acid.

4. With monohydrated nitric acid the oxidation of glycol is still more rapid. Carbonic acid is evolved, and the liquid retains in solution oxalic acid and even a certain quantity of glycolic acid.

From these experiments it appears that the products of the regular and gradual oxidation of glycol are two acids,—glycolic and oxalic acids. The carbonic acid which sometimes appears is produced by the oxidation of oxalic acid itself. The following formulæ express the relations existing between glycol and its products of oxidation:—

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The pure stearine is very white, crystallized in radiate nacreous warts, surmounted by very delicate needles. It fuses at a low temperature into a colourless liquid, and sets on cooling in a puffed-up mass, which presents transparent parts, and white parts as if hydrated; nevertheless they lose nothing in a stove heated to 239° F., and the composition of both parts is the same. The fused stearine is much more transparent than that obtained from tallow; it is very brittle, and furnishes an acid fusing at 158° F. directly by saponification. Its composition is expressed by the formula

$$C^{114}H^{110}O^{12}=3(C^{36}H^{36}O^{4})+C^{6}H^{8}O^{6}-6HO.$$

This would require 95·73 per cent. of stearic acid; the authors have obtained 95·72.

From this it may be deduced that natural stearine is tristearine, as is now admitted by most chemists.—*Comptes Rendus*, June 29, 1857, p. 1355.

On Hydrated Silica and the Formation of Quartz and Opal. *By* O. Maschke.

The gelatinous silica which is precipitated by carbonic acid from a solution of soluble glass, when washed for a sufficiently long time, furnishes a hydrated silica of considerable purity.

Struckmann has recently made experiments upon the solubility of such gelatinous masses. The numbers which, according to Struckmann, express their solubility, do not agree with those obtained by the author. The latter found that in three days 100 parts of water had dissolved 0·09 of silica, and 100 parts of water containing carbonic acid 0·078 of silica. The experiments were made at ordinary temperatures, and the mixtures were frequently agitated.

Gelatinous silica behaves very differently towards water when it is heated therewith for a long time in closed vessels on the water-bath; a complete solution takes place,—nay, even the addition of water is not necessary, as under these circumstances the gelatinous mass liquefies of itself. A liquefied mass of this kind contained 2·49 of silica in 100 parts. The liquefied jelly is not precipitated even by very considerable quantities of alcohol; concentrated saline solutions, however, effect a gelatinization; at least this result is obtained with carbonate of ammonia, chloride of sodium, and chloride of calcium; the alkaline bicarbonates, also, must produce the same effect, as a solution of soluble glass becomes gelatinous by the passage of carbonic acid.

If the liquefied gelatinous mass be left to spontaneous evaporation, a period at last occurs when it becomes thick and syrupous. It then solidifies into a friable transparent mass, which splits up when further dried, and finally forms hard, transparent laminæ, possessing exactly the properties of the noble opal. They dissolve, even after being strongly ignited, completely and readily in a solution of caustic potash or of an alkaline carbonate; they are completely insoluble in water, and adhere strongly to the tongue like clay; they also condense a considerable quantity of gases, for if

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they be thrown into hot water, they hiss at first, and then a large quantity of bubbles are seen rising to the top. When they are exposed to the heat of the hand, for example, in a watch-glass, they soon become turbid, and at length appear like white enamel; this aspect they seem to retain at ordinary temperatures. But if they be more strongly heated, they again become nearly as transparent as before, and if they be then exposed to moist air, they gradually become more and more opalescent; if, on the contrary, they be kept in closed vessels, they retain their transparency. The laminæ which have been ignited exhibit the same behaviour. If the enamel-like pieces be treated with water, they become transparent again instantaneously. The pieces which have been rendered transparent by heating, take up water with great energy and with decrepitation; when the excess of water has been evaporated, the phænomena described may all be produced afresh. An explanation of these peculiarities can only be furnished by the balance and the polarizing apparatus; the author, therefore, abstains from drawing any conclusions.

If gelatinous silica, immediately after washing, be left to spontaneous evaporation, or dried by the employment of a gentle heat, opaline masses are also obtained without any preliminary liquefaction, but these are, at the utmost, only translucent, and exhibit many cracks in their interior; if, on the other hand, it be left standing for several days or weeks in a stoppered bottle, it appears to cake together, and then, by a gentle heat, furnishes opaline fragments of the same beautiful nature as the laminæ above described.

The explanation of the silicatization of plants and the formation of tabasheer, appears from this to present no particular difficulty. Thus, if the water taken up by the plants contains silica and salts in solution, when the juice is concentrated in the plant, a moment must occur when the salts exert a gelatinizing action upon the hydrate of silica; the gelatinous mass dries, and finally forms the opaline mass of which silicatized plants usually consist.

It also appeared easy to prepare quartz and rock-crystal by crystallization from the solution evaporated to the consistence of a syrup; but all these experiments failed, in every case opal alone was formed, although this, swimming about in the fluid in the form of small, narrow laminæ, might easily, by its strong reflexion of light, mislead one into the supposition that crystals were present. The author, therefore, regards the statements of Struckmann and Doveri as incorrect. The well-water, however, in which the thin deposit of quartz had been formed upon the walls of the tubes, and which, besides silica, carbonate of lime and protocarbonate of iron, undoubtedly contained an alkaline carbonate, although only in small quantity, showed another way, which may apparently lead to the desired result.

Thus, if gelatinous silica be dissolved to saturation in a tolerably concentrated, nearly boiling solution of carbonate of potash, all the excess of silica added soon becomes converted into a hard, white mass, which is sandy to the touch. If the solution be allowed to

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author has only observed its action upon nitrate of silver, which is completely reduced either in the cold or by heat by red phosphorus. The reduction is perhaps a little slower than with normal phosphorus, but not less certain.

The ready oxidation of red phosphorus in contact with the air, and its conversion into phosphorous acid at ordinary temperatures, is an important fact, especially considering the attempts made to substitute it for normal phosphorus in matches, with the view of avoiding the numerous accidents to which the latter gives rise. According to Wöhler and Frerichs, 0·5 grm. of phosphorous acid killed a dog in one hour. On the other hand, Bussy, Orfila, and Rigout have completely proved the harmlessness of amorphous phosphorus. But it may be said that this phosphorus would become poisonous by sufficiently long exposure to the air, because it would then give origin to phosphorous acid.

To determine whether this acid was poisonous or harmless, the author administered it to dogs in quantities varying from 0·6 grm. to 1·45 grm. of anhydrous acid. Six dogs were employed; after the injection of the dilute acid into the stomach the œsophagus was tied, and to the author's astonishment, the animals lived for six, eight, and even nine days after the injection of the pretended poison. In each of the six experiments phosphorous acid derived from a special preparation was employed; and for greater exactitude, the quantities of acid were determined by the conversion of bichloride of mercury into protochloride, in accordance with the following equation:—

$$PO^3 + 4HgCl + 2HO = PO^5 + 2Hg^2Cl + 2HCl.$$

The acid was always obtained by the decomposition of protochloride of phosphorus by water, and the liquid evaporated over lime *in vacuo*.

From the above facts it is difficult, or perhaps impossible to attribute a poisonous action to phosphorous acid. The death of the six animals after so long a time is sufficiently explained by starvation, and the consequences of the operation necessary for the ligature of the œsophagus. The author has also ascertained the harmlessness of phosphatic acid, or the mixture of phosphorous and phosphoric acids, produced by the slow combustion of normal phosphorus in moist air.—*Comptes Rendus*, July 20, 1857, p. 113.

On the Composition of the Vegetable Stearine extracted from the Seeds of Brindonia indica. *By* MM. J. Bouis *and* d'Oliveira Pimentel.

As early as the sixteenth century, Garcia da Hortà gave an exact description of the fruit of this tree. The pericarp is used at Goa as a piquant spice; its blood-red acid juice is employed in the preparation of a syrup for refreshing drinks, which is much esteemed by the inhabitants of India. By pressure and hot water a vegetable tallow is extracted from the seeds, which is only used at present in the preparation of some articles of food, friction in some diseases,

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and by the poor for lighting. The authors have obtained from the seeds a pure stearine, furnishing stearic acid fusible at 158° F.

The seeds are of the appearance and size of ordinary French beans; they are very convex and of a reddish-brown colour; they have scarcely any taste, and have a single delicate coat, which is very adherent to the seed. Each seed weighs on an average 0·245 grm.; they contain 1·72 per cent. of nitrogen and 2·58 per cent. deprived of fatty matters.

In the dry state in which the seeds are received, they yield nothing to pressure; when crushed and subjected to the action of aqueous vapour, they soften and furnish on pressure a fatty matter which sets like tallow on cooling. The employment of solvents indicates that the dry seeds contain 30 per cent. of fatty matters. The cake when exhausted by æther is reddish-brown, and yields to alcohol and water or an alkaline solution a colouring matter of a very fine red, which might certainly be used with advantage in dyeing. This is soluble in water and alcohol, insoluble in æther and acids. The crude fatty matter is nearly white, and fuses about 104° F.; it solidifies at a lower temperature. It is insoluble in cold, and sparingly soluble in boiling alcohol. It is easily saponified by lime and by litharge; glycerine, recognizable by all its characters, is left in solution. Potash, and especially soda, saponify it readily, and furnish a soap of excellent quality. The soap when decomposed furnishes well-crystallized fatty acids; one of the acids is liquid and appears to be oleic acid; the other is solid, and constitutes 50 per cent. of the total weight.

The solid acid obtained by pressure and purified by crystallization from alcohol, forms very fine, brilliant, nacreous lamellæ. Its fusing-point is 158° F.; at 156°·56 F. it solidifies into a crystallized mass. Its composition agrees exactly with the formula

$$C^{36} H^{36} O^{4},$$

which is that of stearic acid; this is also confirmed by the analyses and properties of the lead and silver salts, and those of the æther obtained with this acid.

The authors state that the stearine of tallow contains a mixture which it is impossible to isolate. Stearine, prepared with the greatest care by the process of Le Canu, or purified by benzine, by crystallizing a great number of times and separating the mother-liquors, constantly furnished an acid having a point of solidification *inferior* to that of stearine; and it is singular that within certain limits the more the stearine is purified, the less does the acid obtained from it crystallize. All these experimnets confirm Chevreul's results, that the solid acids obtained from tallow are a mixture of two acids.

As the fat of the *Brindonia* furnished pure stearic acid, the authors thought that the same would be the case with the stearine. The latter was obtained by treating the crude fatty matter by the ordinary processes, pressing it well after each crystallization, to get rid of the mother-liquor.

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employed, the black compound is immediately produced, but under the influence of the free acids this becomes white of itself in course of time, and changes to metallic silver. A far greater quantity of the compound of protoxide of silver is, however, produced when the free acids are saturated by a small quantity of a base.—*Bericht der Akad. der Wiss. zu Berlin*, 1857, p. 287.

Compounds of Anthranilic Acid with Acids. *By* W. KUBEL.

Muriate of Anthranilic Acid, $C^{14} H^7 NO^4$, HCl.—Dry anthranilic acid prepared from indigo absorbs dry muriatic acid gas, but it is very difficult to obtain a constant compound in this way. When anthranilic acid is dissolved in concentrated muriatic acid, the new compound crystallizes in fine needles on cooling. Chlorine, calculated 20·46, found 20·44 per cent.

When heated this compound furnishes a crystalline sublimate, which appears from its reactions to be muriate of aniline.

Nitrate of Anthranilic Acid, $C^{14} H^7 NO^4$, NHO^6.—It was obtained by precipitating the preceding compound with 1 atom of nitrate of silver; the filtrate from the chloride of silver, left on evaporation large prismatic crystals, which are readily soluble in boiling alcohol. If 1 atom of the muriate of anthranilic acid be mixed with 2 atoms of nitrate of silver, the filtered fluid, when concentrated, furnishes a compound containing silver, but in smaller quantity than corresponds with the formula $C^{14} H^7 NO^4$, $NHO^6 + NAgO^6$. Nitrate of baryta did not combine with the nitrate of anthranilic acid; the two compounds crystallized separately from their solution.

Sulphate of Anthranilic Acid, $2C^{14} H^7 NO^4$, $S^2 H^2 O^8$.—This was prepared from the muriate with sulphate of silver; it forms needles usually united in concentric groups.

Sulphuric acid, calculated 21·50, found 21·44 per cent.

Oxalate of Anthranilic Acid, $2C^{14} H^7 NO^4$, $C^{14} H^2 O^8$.—Prepared from the muriate with oxalate of silver; it crystallizes in small, silky scales. Oxalic acid, calculated 20·8, found 21·0 per cent.—Liebig's *Annalen*, cii. p. 237.

Observations on Red or Amorphous Phosphorus. *By* J. PERSONNE.

The object of this note is to make known certain facts connected with red phosphorus, which have escaped Schrötter, and at the same time to prove that the eminently poisonous action attributed to phosphorous acid by Wöhler and Frerichs is far from being so certain as those chemists seem to suppose.

Action of the Air.—It is said that red phosphorus remains unaltered in contact with the air, and that it only combines with oxygen at a temperature of about 500° F., at which it becomes converted into ordinary or normal phosphorus. This appears to be true in the case of red phosphorus in tolerably large fragments; but the proof of the contrary is soon obtained by operating with red phosphorus in powder or in small spangles, such as is furnished by

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manufacturing chemists. In this state, without being luminous in the dark, it absorbs oxygen from the air at ordinary temperatures like normal phosphorus, and like this gives origin to an acid liquid containing phosphorous and phosphoric acids. The presence of water greatly facilitates this oxidation. When red phosphorus is moistened daily on a filter with a little distilled water, an acid liquid is obtained every day, which furnishes, with nitrate of silver, a precipitate which soon becomes black. It is even impossible to preserve red phosphorus in spangles, in imperfectly stopped bottles, without its becoming moist in course of time, and sometimes even wet with an acid liquid. Amorphous phosphorus in fragments behaves in the same way in contact with moist air, except that its oxidation is slower in consequence of its cohesion.

To ascertain whether this oxidation is due to the red phosphorus, or to the slow conversion of the red phosphorus into normal phosphorus, the author placed in several closed tubes a certain quantity of red phosphorus completely freed from normal phosphorus by repeated washing with boiling sulphuret of carbon; these tubes were left in a hot-house, with a temperature of 77° to 86° F. for two months. On opening these tubes at different periods, not the slightest trace of normal phosphorus could be separated by sulphuret of carbon, nor was there the least phosphorescence in the dark. This phosphorus, however, when exposed to moist air, soon became acidified, which proves that red phosphorus actually absorbs oxygen from the air.

Action of Chlorine.—According to Schrötter, chlorine combines with red phosphorus at ordinary temperatures with evolution of heat, but without production of light, furnishing at first protochloride and afterwards perchloride; and it is only by heating red phosphorus in a current of chlorine that it can be inflamed. The author states that if red phosphorus in spangles be placed in a small tubulated retort, furnished with a cooled receiver, and a current of chlorine at the ordinary temperature be passed over the surface of the phosphorus, the latter becomes ignited at its contact with the jet of gas, without production of flame; it burns like German tinder, and the ignition follows the jet of gas. There is therefore a production of light. No trace of protochloride was observed. Perchloride alone was formed, and this may be understood, as the action is concentrated and as it were exhausted upon one point of contact before becoming extended to neighbouring portions; the chlorine is consequently always in excess.

Nitric Acid.—Nitric acid dissolves red phosphorus, whether cold or hot, producing nitrous vapours, and phosphorous and phosphoric acids, as with normal phosphorus. This solution takes place with so much ease that the author proposes in the preparation of tribasic phosphoric acid to substitute red phosphorus for normal phosphorus, the solution of which in nitric acid is always tedious when the acid is weak, and dangerous when it is concentrated.

Metallic Salts.—According to Schrötter, red phosphorus neither precipitates copper, nor the other metals from their solutions. The

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$$\underbrace{\left.\begin{matrix}C^4H^4\\H^2\end{matrix}\right\}O^4}_{\text{Glycol.}}, \qquad \underbrace{\left.\begin{matrix}C^4H^2O^2\\H^2\end{matrix}\right\}O^4}_{\text{Glycolic acid.}}, \qquad \underbrace{\left.\begin{matrix}C^4O^4\\H^2\end{matrix}\right\}O^4}_{\text{Oxalic acid.}}.$$

These relations are the same that exist between alcohol and acetic acid:—

$$\underbrace{\left.\begin{matrix}C^4H^5\\H\end{matrix}\right\}O^2}_{\text{Alcohol.}}, \qquad \underbrace{\left.\begin{matrix}C^4H^3O^2\\H\end{matrix}\right\}O^2}_{\text{Acetic acid.}}.$$

In both cases the products of oxidation are formed by the substitution of oxygen for a certain quantity of the hydrogen of the alcoholic radical. The radical of glycol is olefiant gas; oxygen enters into this radical by substitution, and when the substitution is complete oxalic acid is formed. If, for the conversion of monoatomic alcohol into acetic acid, 4 equivs. of oxygen are required, diatomic glycol must require 8 equivs. to undergo a corresponding transformation:—

$$\underbrace{C^4H^6O^4}_{\text{Glycol.}}+O^8=4HO+\underbrace{C^4H^2O^8}_{\text{Oxalic acid.}}.$$

Thus it might be said that oxalic acid is the acetic acid of glycol. Glycolic acid is an intermediate, less oxidized product.

These experiments prove certainly that oxalic acid contains 4 equivs of carbon, for, being derived from glycol, it originates definitively from olefiant gas which contains 4 equivs of carbon.

These facts will probably not remain isolated. There are other organic acids belonging to the same series as oxalic acid, containing like it 8 equivs. of oxygen, and carbon and hydrogen combined in the same proportions. These are succinic, adipic, lipic, suberic, and sebacic acids. Just as oxalic acid is derived from glycol, these acids, which are higher in the series, and which have hitherto been isolated, belong to superior glycols, the existence of which the author has proved. The following formulæ express the relations existing between the glycols and the acids produced by their oxidation:—

$\underbrace{C^2H^4O^4}_{\text{Methyloglycol.}}$,	$\underbrace{C^2H^2O^6}_{\text{Carbonic acid.}}$.	
$\underbrace{C^4H^6O^4}_{\text{Glycol.}}$,	$\underbrace{C^4H^4O^6}_{\text{Glycolic acid.}}$,	$\underbrace{C^4H^2O^8}_{\text{Oxalic acid.}}$.
$\underbrace{C^6H^8O^4}_{\text{Propyloglycol.}}$,	$\underbrace{C^6H^6O^6}_{\text{Lactic acid.}}$,	$\underbrace{C^6H^4O^8}_{\text{Acid unknown.}}$.
$\underbrace{C^8H^{10}O^4}_{\text{Butyloglycol.}}$,	$\underbrace{C^8H^8O^6}_{\text{Acid unknown.}}$,	$\underbrace{C^8H^6O^8}_{\text{Succinic acid.}}$.

Comptes Rendus, June 29, 1857, p. 1306

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On the Behaviour of Protoxide of Iron towards Oxide of Silver.
By H. Rose.

When a solution of protosulphate of iron is mixed with a solution of nitrate of silver, the silver is separated in a metallic form. The result, however, is different when the peroxide of iron formed from the protoxide cannot combine with sulphuric and nitric acids.

Thus, if moist oxide of silver be added in sufficient quantity to a solution of protosulphate of iron, the former becomes deep black, but is still converted into metallic silver after some time, and only acquires greater stability when the quantity of oxide of silver is very predominant. The filtered fluid then contains no iron, but sulphate of silver.

The black compound is obtained most readily and of the greatest stability when a solution of nitrate of silver is mixed with so much ammonia that the small quantity of oxide of silver separated is again dissolved, and an excess of this fluid is dropped into a solution of protosulphate of iron. A deep black precipitate is then formed immediately, possessing a remarkably strong colouring power, so that the smallest quantities of protoxide of iron, as also of oxide of silver, may be detected in this way. In the first case, the slightly ammoniacal solution of oxide of silver is as sensitive a reagent as the solutions of ferrocyanide of potassium and sulphuret of ammonium.

The black precipitate is very stable and undergoes no change in the air. At a dull red heat it only loses water, but otherwise experiences no change of composition; at a stronger red heat it is converted into metallic silver and peroxide of iron. By trituration in an agate mortar it acquires a metallic lustre. By dilute muriatic acid it is converted into chloride of silver, metallic silver, and sesquichloride of iron; but the quantity of metallic silver separated is not very considerable. It is greater when the compound is treated with dilute acetic acid. By nitric acid peroxide of iron is first separated, whilst silver dissolves with evolution of gas; complete solution takes place on the application of heat. When treated with solution of perchloride of gold, chloride of silver is formed with separation of metallic gold.

The compound formed by different preparations is of the same composition. It consists of 1 atom of protoxide of silver, 2 atoms of protoxide of iron, and 1 atom of peroxide of iron, which has taken the place of an acid towards the two bases.

A compound of 1 atom of protoxide of silver and 1 atom of peroxide of iron, without protoxide, may however be obtained by dissolving oxide of silver in ammonia and adding to this solution one of protosulphate of iron, the solution of oxide of silver being present in great excess.

When protoxide of iron and oxide of silver are combined with weak acids, the solutions of these neutral compounds form the black precipitate of protoxide of silver, without the addition of ammonia or any other base. If protacetate of iron and acetate of silver be

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	No. 1.	No. 2.
Phosphate of magnesia	0·190	0·182
corresponding with		
Phosphate of lime	0·262	0·251
Whence for 100 parts of material	5·2	5·0

Thus this substance, which 3 months before was scarcely soluble in weak acetic acid, became very soluble in this liquid by the influence of the air alone. It nevertheless continued completely insoluble in carbonic acid.

Action of weak Acetic and Carbonic Acids combined on the Powder of the Nodules.—One gramme of nodules from the Ardennes and 1 gramme from Arcyfay were placed in 20 cub. cent. of weak acetic acid; carbonic acid washed in bicarbonate of soda was passed in; there were dissolved in—

	100 of powder from the Ardennes, exposed to the air for 3 months.		100 of powder from Arcyfay, not exposed to the air.	
	No. 1.	No. 2.	No. 1.	No. 2.
Phosphate of lime	8·8	8·9	3·4	5·1
Oxide of iron and alumina...	0·6	0·6	traces	traces
Carbonate of lime	16·3	16·3	0·39	1·2

In another series of experiments under less favourable conditions of solubility, acetic acid of 1·035 sp. gr. and carbonic acid dissolved in—

	100 of animal charcoal.		100 of nodules from the Ardennes, exposed to the air for 1 month.		100 of nodules from the Ardennes, calcined.	
	No. 1.	No. 2.	No. 1.	No. 2.	No. 1.	No. 2.
Phosphate of lime	24·4	26·9	4·9	6·0	4·4	4·4
Oxide of iron and alumina	...	...	0·2	...	0·7	0·7
Carbonate of lime	8·5	7·6	1·7	0·41	1·6	1·4

From these experiments the author draws the following conclusions:—

The nodules of phosphate of lime reduced to a fine powder are always but slightly soluble in carbonic acid; slightly soluble at first in weak acetic acid, but more soluble after being exposed to the air for some time; always perceptibly soluble in acetic and carbonic acids combined, and the more so the longer they have been exposed to the air. As regards the efficacy of these phosphates as manure, their insolubility in carbonic acid tends to prove that they can be of no use in soils in which this acid exists alone, unless they are previously acted upon by strong acids. The solubility of the native phosphates in acetic and carbonic acids combined seems to show that when simply reduced to powder, they may be usefully employed in a soil with an acid reaction, such as cleared heaths which contain these two acids, or carbonic acid and another capable of playing the part of acetic acid.—*Comptes Rendus*, July 6, 1857, p. 13.

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ANALYTICAL CHEMISTRY.

On a new Method of separating Oxide of Cadmium from Oxide of Zinc. By C. AUBEL *and* G. RAMDOHR.

THE property possessed by tartaric acid, of preventing the precipitation of the metallic oxides by fixed caustic alkalies, is very general. We have tested the behaviour towards caustic potash or soda, of the oxides of most frequent occurrence, both of the metals which do and those which do not decompose water. The experiments were made by mixing as neutral a solution as possible of the oxides in HCl or NO^5 with an excess of tartaric acid in solution, and then with a sufficient quantity of solution of caustic soda of spec. grav. 1·161 to 1·191 (containing 10 to 12 per cent. of solid caustic soda), to produce a distinctly alkaline reaction. With but few exceptions all the metallic oxides may be obtained in alkaline solution, by the employment of a sufficient quantity of tartaric acid. The solubility varies, so that the oxides require for their solution, different quantities of tartaric acid and NaO. It is, however, easy to hit the right point for obtaining a perfectly clear alkaline solution of most metallic oxides.

The property possessed by some of these alkaline solutions of metallic oxides, of being precipitated by a boiling heat, is well worthy of notice. Although the solubility of some metallic oxides in NaO or KO in the presence of tartaric acid has already been practically applied in many analytical operations, no one yet appears to have thought of employing the precipitability at a boiling heat in analysis. Most of the alkaline solutions remain perfectly clear at this temperature, but some are very soon thrown down in the form of hydrated oxides, or reduced to the metallic state. This behaviour may be made use of in many cases for qualitative analysis, and for quantitative separation and determination. The complete precipitation of those oxides which are thrown down by boiling, is greatly dependent upon the concentration of the fluid. The more dilute the solution, the more rapidly and completely are the oxides generally precipitated.

We were led to follow the subject further especially by the solubility of oxide of cadmium in NaO in the presence of tartaric acid; we obtained the following results:—

Pure metallic cadmium was dissolved in NO^5, a sufficient quantity of tartaric acid was added, and then solution of soda; the solution was finally diluted with pure water and boiled. The CdO was precipitated in white flakes as CdO, HO, and after the boiling was continued for 1½ to 2 hours, no more oxide of cadmium remained in solution. To make sure that the precipitate of CdO, HO was free from alkali, it was dissolved in the smallest possible quantity of NO^5, and the solution, when greatly diluted with water, precipitated by sulphuretted hydrogen. The filtrate from the CdS left no residue when evaporated. Quantitative analysis also showed that the alkaline solution of oxide of cadmium is completely precipitated by boiling.

0·8835 grm. of CdO were dissolved in HCl, 15 grms. of solution of tartaric acid (containing 0·230 grm. of crystallized tartaric acid in the gramme) were added to it, and it was then mixed with

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2. Propylene heated for seventy hours to 212° F. with an aqueous solution of muriatic acid, is completely absorbed and gives origin to propylo-muriatic æther. This body is formed by propylene and muriatic acid gas in equal volumes,—

$$C^6 H^6 + HCl = C^6 H^7 Cl.$$

The combination takes place even at ordinary temperatures, but much more slowly, and it is not accelerated by continued agitation. Under the same circumstances the author also combined hydrobromic and hydriodic acids with propylene, producing propylhydrobromic and propylhydriodic æthers.

The gaseous carburet is heated to 212° F. in sealed balloons, with an aqueous solution of the hydracids saturated in the cold, and employed in great excess. The æthers are purified by distillation, after being agitated with an aqueous solution of potash.

3. The preceding results may be generalized. Amylene, $C^{10} H^{10}$, combines with muriatic and hydrobromic acids under the same conditions, although more slowly and in a less complete manner, forming amylomuriatic and amylhydrobromic æthers, $C^{10} H^{11} Cl$ and $C^{10} H^{11} Br$.

4. Caprylene, $C^{16} H^{16}$, gives rise to the same reactions, but the combination remains incomplete even after 100 hours of contact at 212° F.; the æthers formed are purified by distillation. If caprylene and muriatic acid gas are brought in contact at the ordinary temperature, the hydrocarbon immediately absorbs seven or eight times its volume of the gas; the absorption then continues gradually diminishing, and is not increased sensibly by long-continued agitation. In two hours it was equal to 10 volumes; in five days to 12 volumes; in eleven days to 13 volumes; in seventeen days to 14 volumes; in twenty-three days to 15 volumes, &c.

5. Æthalene, $C^{32} H^{32}$, behaves similarly, both at the ordinary temperature and at 212° F. At the latter temperature, after 100 hours of reaction, nearly half the hydrocarbon is combined with the hydrobromic (or muriatic) acid in the form of a neutral compound. The æthers formed could not be separated from the excess of hydrocarbon, because the heat necessary to distil them causes their decomposition.

6. Olefiant gas, $C^4 H^4$, heated to 212° F. for 100 hours, with an aqueous solution of hydrobromic acid saturated in the cold, is completely absorbed; a neutral liquid like or identical with hydrobromic æther is formed. Under the same circumstances muriatic acid only furnishes traces of a neutral chlorinated compound.

Thus the various hydrocarbons corresponding to the alcohols, and formed of equal equivalents of hydrogen and carbon, can combine directly and in equal volumes with the hydracids, whence results a new relation between the æthers and the ammoniacal salts. The hydrobromic æthers decomposed by salts of silver, furnish the compound æthers, and consequently the alcohols. By these methods, therefore, the hydrocarbons may generally be converted into the æthers and alcohols corresponding with them.—*Comptes Rendus*, June 29, 1857, p. 1350.

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On the Solubility of the Fossil Phosphates of Lime in the Acids of the Soil. *By* M. DEHERAIN.

The author's experiments had reference to the action of—

1. Carbonic acid;
2. Acetic acid;
3. Acetic and carbonic acids combined.

The powders experimented on contained in 100 parts after desiccation:—

	Animal charcoal.	Nodules from the Ardennes. Uncalcined mixtures from various beds.			Nodules from Arcyfay, uncalcined.		Nodules from the Ardennes. Various beds, calcined.	
		No. 1.	No. 2.	No. 3.	No. 1.	No. 2.	No. 1.	No. 2.
Phosphate of lime ...	58·7	46·4	46·4	44·3	40·6	40·2	42·2	40·7
Carbonate of lime ...	4·5	13·4	14·7	16·2	6·7	lost	13·2	15·3
Oxide of iron	...	3·9	3·7	2·4	4·2	4·3	9·6	8·2
Alumina	...	1·2	1·3	1·1	1·4	1·3	4·6	5·6

Action of Carbonic Acid upon the Powder of Nodules from the Ardennes, not calcined.—A gramme of powder of nodules from the Ardennes, uncalcined, that is not submitted to the successive action of fire and water, was placed in a small bottle with distilled water and carbonic acid passed in for about twenty minutes; the acid was produced by the action of muriatic acid upon white marble, and washed in a solution of bicarbonate of soda. After standing for 48 hours, it was filtered, and on adding oxalate of ammonia, there was found

	No. 1.	No. 2.
Carbonate of lime....	11·2	11·3.

By adding ammonia, and then oxalate of ammonia, only a very slight opalescence was obtained.

Five grammes of the same powder treated in the same way, but filtered in 24 hours, only gave carbonate of lime and no phosphate. This powder was, however, in a state very favourable for solution.

The attempt to dissolve the calcined and slaked nodules from the Ardennes in carbonic acid was also vain; lime is dissolved but no phosphates.

Action of Acetic Acid of 1·035 *sp. grav. upon the Powder of the Nodules.*—In trying to dissolve *recently pulverized* nodules in weak acetic acid, the precipitates are in general very slight, even in operating upon several grammes of material; but this is not the case in treating phosphates which have been *reduced to powder for some time.*

Powder of nodules from the Ardennes left with weak acetic acid in an open bottle for 3 months, was found to have fixed water; it contained 17·6 per cent., instead of 2·5 to 6 per cent., which is the average amount in the powdered nodules. 5 grms. were put into acetic acid of 1·035 sp. grav., and filtered in 24 hours; the temperature had not exceeded 68° F. The filtrate gave

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with solution of potash for the removal of the chlorine, dried over chloride of calcium and rectified. The distillate is limpid, has a pleasant odour, like that of oil of bitter almonds, and a spicy taste, makes a greasy spot upon paper which again disappears; it is scarcely soluble in water, but dissolves readily in alcohol and æther, and boils at 266–270° F. This substance contains chlorine; it is consequently a mixture of valeronitrile and chlorovaleronitrile,—

$$x\,C^{10}H^{9}N + y\,C^{10}H^{8}ClN,$$

as appears from the following analyses:—

I.

	Found.		Chlorovaleronitrile.		Valeronitrile.		Per-centage Comp.
C	63·51	=	22·95	+	40·56	or	72·66
H	9·70		3·06	+	6·64		11·89
Cl	13·58		13·58				
N	13·96		5·35	+	8·61		15·45

II.

C	66·93	=	14·67	+	52·26	or	72·78
H	9·90		1·95	+	7·95		11·06
Cl	8·68		8·68				
N	15·01		3·42	+	11·59		16·16

Valeronitrile requires—

C	10	=72·29
H	9	10·84
N	1	16·87.

In the retort there remains an acid solution, which deposits white crystals when concentrated. These are a compound of 2 atoms of leucine with 1 atom of muriatic acid.

$$2C^{12}H^{13}NO^{4}, HCl.$$

Compounds of glycine and alanine of a similar constitution are already known.

During the passage of the chlorine a crystalline yellow body sometimes separates, the nature of which could not be more exactly investigated from want of material.

When chlorine is passed over dry leucine, kept cold with ice, the leucine acquires an increase of weight of 27·1 to 27·4 per cent., and becomes at the utmost of a pale yellowish colour. Carbonic acid is evolved. The following formula shows the reaction:—

$$7(C^{12}H^{13}NO^{4}) + 8Cl = \left\{\begin{matrix} 6(C^{12}H^{13}NO^{4}, HCl) \\ C^{10}H^{7}Cl^{2}N \end{matrix}\right\} + C^{2}O^{4},$$

as is proved by analysis. The entire amount of chlorine is 24·6 per cent., of which, however, only 18·4 per cent. is present as muriatic acid.

	Calculated.	Found.	
As muriatic acid	18·4	18·2	18·7 per cent. chlorine.
Total chlorine..	24·6	25·8	24·5 „ „

Water therefore takes no part in the decomposition of leucine by chlorine.

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4. *Bromine* acts in the same way as chlorine.

5. *Iodide of æthyle*, heated to 230° F. in closed tubes with leucine, dissolves the latter slowly, forming a brown syrupous fluid, which is soluble in alcohol, and furnishes unaltered leucine again. Hydrogen is not replaced in it by æthyle.

In consequence of this behaviour of leucine, the author places it in the same group with carbanilic or anthranilic acid, and regards it as probable that it is *amylocarbaminic acid*. The following equations illustrate this:—

$$\underset{\text{Leucine.}}{C^{12}H^{13}NO^4} = \underset{\text{Amylocarbaminic acid.}}{\left.\begin{matrix}N(C^{10}H^{11})(C^2O^2)\\ H\\ H\end{matrix}\right\}O^2} = \underset{\text{Amylamine.}}{C^2O^4 + C^{10}H^{13}N}$$

$$\underset{\text{Anthranilic acid.}}{C^{14}H^7NO^4} = \underset{\text{Carbanilic acid.}}{\left.\begin{matrix}N(C^{12}H^5)(C^2O^2)\\ H\\ H\end{matrix}\right\}O^2} = \underset{\text{Aniline.}}{C^2O^4 + C^{12}H^7N}$$

The formation of valeronitrile is explained by an abstraction of hydrogen by chlorine. The muriatic acid produced attacks still undecomposed leucine, which then undergoes no further alteration. If chlorine be passed into a solution of leucine in potash, the muriatic acid attacks the potash, and thus a large quantity of valeronitrile is obtained.

By treatment with nitrous acid leucine and anthranilic acid furnish leucic and salicylic acids, which are consequently to be regarded as corresponding members of different series.

Sulphuric acid does not, as might have been expected, furnish with leucine sulphamylamic acid (corresponding with sulphanilic acid), but valeral, carbonic acid, ammonia, and sulphurous acid; this reaction is, however, very easily explained by the above formula. —Liebig's *Annalen*, cii. p. 221.

On the direct Combination of the Hydracids with the Alcoholic Hydrocarbons. *By* M. Berthelot.

1. In a memoir published two years ago, the author showed that olefiant gas can fix the elements of water and become the source of alcohol: $C^4H^4 + 2HO = C^4H^6O^2$. Propylene, C^6H^6, may undergo the same transformation, and become propylic alcohol, $C^6H^8O^2$. In extending this reaction to the various hydrocarbons of the alcohols, the author was obliged to have recourse to processes distinct from those first employed, substituting the hydracid for sulphuric acid. The conversion of olefiant gas into alcohol, and of propylene into propylic alcohol, alone succeeded perfectly with sulphuric acid; but this acid cannot be employed with hydrocarbons of a high equivalent, upon which it acts too energetically, sometimes carbonizing them, sometimes modifying them isomerically. Caprylene, $C^{16}H^{16}$, mixed with concentrated sulphuric acid, gives origin, in the first place, to a homogeneous liquid, not without a brisk evolution of heat, but the modified hydrocarbon soon separates and floats, whilst the acid only retains traces of organic matter in solution. These phænomena resemble the reaction of sulphuric acid upon turpentine.

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cool, it solidifies into a white, non-gelatinous mass (dilute solutions, on the contrary, become gelatinous), which gradually sinks, and may be pressed together. If this be washed after the carbonate of potash has been squeezed out as far as possible by frequent pressure with a spatula, the silica is obtained after drying in the form of a white, very soft, but conglomerated powder, which exhibits molecular movements under the microscope. This silica does not dissolve in water, but it is soluble in a solution of carbonate of potash, which must naturally be the case, as even finely powdered rock-crystal is dissolved in considerable quantities by solution of carbonate of potash.

If the saturated solution be evaporated at the same temperature at which the solution took place, it remains clear, but the silica separates on the surface of the fluid in the form of a perfectly transparent film, which adheres with uncommon readiness even to a platinum spatula, and may be kneaded together below the surface of the fluid into a translucent lump; small fragments of this become perfectly transparent when kept for some time in the hot fluid. But if such masses be thrown into water, they break up into a coarse powder which is sandy to the touch, and readily soluble in solution of carbonate of potash; this is a matter of course, as the kneaded masses begin to dissolve again in the fluid, as soon as the evaporated water is replaced.

The author varied this experiment by sealing up this coarse powder in a glass tube with a solution of silica in carbonate of potash saturated at the boiling-point of water, and heating it for 8 days in the water-bath. At the end of this time the silica was for the most part only caked together, although small portions had also become quite transparent; when boiled with Liq. Kali carbon. (Pharm. Bor.), it dissolved with far more difficulty; the molecules of the silica had therefore become more approximated by the long-continued heat.—*Archiv der Pharm.*, cxl. p. 37.

On some Decompositions of Leucine. *By* H. Schwanert.

For the preparation of the leucine employed in the following investigation, 2 pounds of horn-shavings were boiled for 24 hours with a mixture of 2 pounds of English sulphuric acid, and 13 pounds of water, the water evaporated being constantly replaced. The filtrate was mixed with lime until it had an alkaline reaction; it was then filtered, evaporated to 12 pounds, and the lime precipitated by oxalic acid; it was again filtered and evaporated till it formed a crystalline film. The yellowish laminæ and granules, grouped in the form of druses, which separated, consisted of leucine with a little tyrosine. The leucine was obtained in perfectly white laminæ, by recrystallization, solution in so much hot water that only a small portion (tyrosine) separated on cooling, decolorization with animal charcoal, evaporation and repeated recrystallization from alcohol.

This mode of preparation is the most advantageous; when the acid

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is more or less diluted, the results are less satisfactory. By boiling the fluid saturated with lime for 24 hours with the sulphate of lime, as recommended by von Hinterberger, the author did not obtain any more leucine, nor did he observe any decolorization of the fluid.

1. *Action of high Temperatures.*—When carefully heated, leucine sublimes without fusion; with a stronger heat, as observed by Proust and Braconnot, it fuses and furnishes a yellow, oily distillate which at last becomes solid. This takes place principally at 356° F. The distillate when treated with muriatic acid (when carbonic acid is evolved), evaporated, dissolved in absolute alcohol, and again evaporated, deposits large flat prisms, which are fatty to the touch, and are readily soluble in water and alcohol. If the aqueous solution be mixed with concentrated solution of potash, an oily stratum separates, which may be purified by distillation. It has a strongly alkaline reaction, and smells at once like ammonia and fusel oil; it is lighter than water, and boils at 206°·6 F. This fluid is *amylamine*. When neutralized with muriatic acid and treated with bichloride of platinum, it furnishes a precipitate consisting of yellow laminæ of the formula $C^{10} H^{13} N HCl, PtCl^2$.

	Found.		Calculated.
Platinum	33·5	33·67	33·66

If the small quantities of empyreumatic oil and ammonia in the distillate, and the residue in the retort, be regarded as secondary products, leucine is decomposed at 356° F. into *carbonic acid* and *amylamine*.

2. *Action of Sulphuric Acid.*—Fuming sulphuric acid dissolves leucine, and the solution is colourless in proportion as heat has been avoided. By precipitating with carbonate of baryta and evaporating the filtrate, the leucine separates unaltered in crystals. Anhydrous sulphuric acid is rapidly absorbed by dry leucine; a moderate heat is produced and a brown, inodorous, thick fluid solution is formed, from which, when long heated to 212° F., carbonic acid and sulphurous acid are evolved with strong effervescence. After treatment with carbonate of baryta, as above, far less leucine is obtained. If the solution of leucine in anhydrous sulphuric acid be heated to 212° F., and mixed with water, a fruit-like odour is perceived, and by distillation a fluid is obtained, which, when completely purified, is limpid and very mobile, boils at 206°·6 F., burns with a luminous flame, dissolves easily in alcohol and æther, and sparingly in water, and when agitated with an alkaline bisulphite solidifies into a white crystalline mass. This is the aldehyde of valerianic acid, $C^{10} H^{10} O^2$.

C	69·2	10	69·8
H	11·6	10	11·6
O	..	2	18·6

3. *Action of Chlorine.*—If chlorine be passed into a retort containing a mixture of leucine with 2 parts of water, carbonic acid is evolved, and an oily fluid separates. This is distilled over, agitated

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20 grms. of solution of soda of spec. grav. 1·11 and 60 grms. HO. The CdO, HO thrown down by several hours' boiling weighed, after ignition, 0·8843. Calculated for 100 parts this gave—

Employed.	Found.
100·000	100·090.

As oxide of zinc in alkaline solution is not precipitated by boiling (even in the presence of tartaric acid), we attempted to effect the quantitative separation of CdO from ZnO by means of this property; by the analysis we obtained such closely concordant numbers that it is easy by this means to separate these two metallic oxides quantitatively and completely. The method is more easily carried out than the separation by means of HS from an acid solution, and the two oxides are more completely separated than by HS. In the application of this new method, it is necessary to employ neutral solutions of the oxides in HCl or NO^5, and then to add sufficient tartaric acid and so much KO or NaO as to give a distinctly alkaline reaction. It is also requisite to dilute it with a sufficient quantity of water, because otherwise the CdO is not completely thrown down.

We obtained the following results by quantitative analysis:—

I. 0·2755 grm. of pure, freshly calcined oxide of zinc and 1·0193 grm. of pure, calcined CdO were dissolved in as little HCl as possible, and 15 grms. of solution of tartaric acid, containing 0·230 grm. of crystallized acid in the gramme, 35 grms. of solution of soda of spec. grav. 1·16, and 85 grms. of distilled water were added. The solution was boiled continuously for 2 hours. The precipitate of CdO, HO produced was collected upon a filter, completely washed, dried, and then removed from the filter, and ignited in a porcelain crucible. The filter was burnt by itself upon a platinum wire, and the ashes added to the calcined CdO. In this way we obtained 1·0191 CdO.

The alkaline solution of zinc filtered away from the CdO, HO was precipitated with sulphuretted hydrogen, the ZnS was dissolved in HCl, and the solution of chloride of zinc was poured into a boiling solution of NaO, CO^2. The resulting precipitate of basic carbonate of zinc was collected upon a filter, washed, dried, and calcined like the CdO. We obtained 0·2733 ZnO.

II. 0·2490 grm. ZnO and 0·5790 CdO, dissolved as before in HCl, mixed with 20 grms. of solution of tartaric acid of the same concentration as in Analysis I., 45 grms. of solution of soda of spec. grav. 1·16, and 100 grms. HO, and then boiled for 2 hours, furnished after the same treatment as in I., 0·2550 ZnO and 0·5758 CdO.

III. 0·9795 grm. ZnO and 1·2570 CdO dissolved in HCl, mixed with 30 grms. of solution of tartaric acid (0·230 grm. of tartaric acid in the gramme), 50 grms. of solution of soda of spec. grav. 1·16, and 120 grms. HO, and boiled for 2 hours, furnished 0·9743 ZnO and 1·2533 CdO.

IV. 0·6280 grm. ZnO and 0·8364 CdO dissolved in HCl, mixed with 20 grms. of solution of tartaric acid of the same strength, 50 grms. of solution of soda of spec. grav. 1·16, and 200 grms. HO, and boiled for 2 hours, furnished 0·8349 CdO and 0·6195 ZnO.

If these numbers be calculated for 100 parts, we obtain for the preceding analyses the following results:—

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	Synthesis.	Analysis.
I.	21·277 ZnO.	21·146
	78·722 CdO.	78·853
	99·999	99·999
II.	30·072 ZnO.	30·693
	69·927 CdO.	69·222
	99·999	99·915
III.	43·796 ZnO.	43·840
	56·204 CdO.	56·203
	100·000	100·043
IV.	42·884 ZnO.	42·601
	57·116 CdO.	57·407
	100·000	100·008

Besides these analyses several others were effected in which metallic cadmium and metallic zinc were employed. The solutions were prepared in the same way as in the preceding analyses, but with this difference, that they were only diluted with a little water. This was the reason why the separation was not so complete as when a greater dilution was employed. The oxide of zinc produced under these circumstances from the alkaline solution after the precipitation of the CdO, HO by boiling generally contained cadmium, so that the amount of zinc appeared to be too high.

A simplification of the separation may probably be introduced by saturating the solution, freed from CdO by boiling, with gaseous CO^2, by which means the ZnO is precipitated. We have not yet been able to complete the experiments in this direction.

As peroxide of copper is not precipitated from its alkaline solution in the presence of tartaric acid, cadmium may be detected in the presence of copper by mixing the acid solution of the two oxides with tartaric acid and KO or NaO until strong alkaline reaction, and boiling for a considerable time. The cadmium is precipitated as CdO, HO, and even small quantities of cadmium may be easily recognized in the presence of copper.

On testing the metallic oxides of most frequent occurrence as to their behaviour towards KO or NaO in the presence of tartaric acid, we observed that they may be arranged in three groups, according to their solubility or insolubility in the cold on the one hand, and on the other, according to their precipitability from the alkaline solution by boiling.

1. Those metallic oxides which are soluble in KO or NaO in the presence of tartaric acid, and are not precipitable from the alkaline solution by boiling, are the following:—

Al^2O^3; Be^2O^3; ZnO; Fe^2O^3; NiO; CoO; Cr^2O^3; PtO^2; PbO; Bi^2O^3; CuO.

2. Those which are precipitable by boiling the alkaline solution when sufficiently diluted with water, are

MnO; CdO; Ur^2O^3 (AuO^3 is dissolved, but is reduced by boiling in the form of a beautiful metallic speculum, which is deposited on the sides of the test-tube).

3. The following cannot be obtained in alkaline solutions in the presence of tartaric acid:—

SnO (a black precipitate is produced in the cold, and this increases by boiling, and soon settles to the bottom); HgO; AgO (is reduced, on boiling the mixture, as a metallic speculum, without previous solution).

Liebig's *Annalen*, July 1857, p. 33.

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THE CHEMICAL GAZETTE.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Silicium and the Metallic Siliciurets.

By MM. SAINTE-CLAIRE DEVILLE *and* CARON.

A CHARACTER common to all the metals is the property of dissolving in each other and forming the peculiar combinations known as *alloys*. Alloys behave as true solutions of one metal in another, like aqueous solutions, from which by alterations of temperature, or by evaporation, we may obtain either hydrated compounds, or the dissolved matter in a pure state. This observation applies to some metalloids, —carbon, boron, and silicium, which in this respect behave like metals. By this means graphite, boron, and silicium have been prepared by extracting them from true alloys.

Silicium is capable of crystallizing in the midst of aluminium. Zinc is another solvent of silicium, and from its volatility may be a valuable material in another point of view. Simple bodies dissolved in this metal may be extracted therefrom by the solution of the zinc by acids, when they are unalterable by those agents, and by the evaporation of the zinc when they are non-volatile.

The preparation of silicium by means of zinc is very easy, and enables considerable quantities of silicium of the finest form to be obtained at a small cost. An earthen crucible is heated to redness, and a mixture of 8 parts of fluosilicate of potash, 1 part of sodium, cut into small fragments, and 1 part of granulated zinc is poured into it. A very slight reaction accompanies the reduction of the silicium, and would not be sufficient to cause the complete fusion of the materials. The crucible must therefore be heated to redness. and kept at this temperature until the scoria is completely fused, The heat must not be carried so high that the zinc might be volatilized. It is allowed to cool slowly, and when the solidification is complete, the crucible is broken. It contains an ingot of zinc penetrated throughout, but especially in the upper part, by long needles of silicium. They are chaplets of regular octahedra, often wedge-shaped, inserted one into the other parallel to the axis which unites the summits of two opposite angles. Most of these crystals only present the angle 109° 28′. To extract them, the zinc is dissolved in muriatic acid, and they are boiled in nitric acid.

In this way very fine and voluminous crystals of silicium are ob-

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tained, in larger quantity than by any other method. It appears that the zinc does not retain much silicium at the moment of its solidification; the liquids only furnished traces of silica or graphitoid silicium, and the only portion of silicium that is lost, is that which may be evolved in the form of the siliciuretted hydrogen of Wöhler and Buff during the solution of the zinc.

If the zinc and silicium be heated to a temperature far higher than that of the vaporization of the metal, the silicium remains as a fused substance completely free from zinc. The silicium itself then fuses into a mass, which during its solidification acquires all the crystallographic characters of fused silicium. Pure silicium may be fused and run into moulds.

Silicium and iron furnish several kinds of cast iron or steel which are exceedingly fusible, and in which silicium plays the part of carbon.

Siliciuret of Copper or *Copper-steel.*—When silicium is prepared with chloride of silicium and sodium in copper trays, the latter are covered with a stratum of white metal, hard enough to resist the file; this is a siliciuret of copper which may be easily prepared even on a considerable scale. A very hard alloy, brittle and white like bismuth, and containing 12 per cent. of silicium, is obtained by fusing together 3 parts of fluosilicate of potash*, 1 part of sodium, and 1 part of copper turnings at such a temperature that the metallic bath may be covered by a very fluid scoria. The copper takes up a considerable proportion of the silicium set free in this operation, and remains in the form of a white matter more fusible than silver, which may be employed for the production of other alloys.

The alloy with 4·8 per cent. of silicium possesses a fine bright bronze colour. It is a little less hard than iron, which it resembles exactly in its behaviour to the file, the saw, and the lathe, whilst ordinary bronze, which is much softer, clogs the tools. Its ductility is perfect; its wire possesses a tenacity at least equal to that of iron. It is as fusible as common bronze.

The other alloys become harder as the amount of silicium increases, but at the same time they lose ductility. The silicium is always distributed uniformly throughout the mass; the alloys are homogeneous and not capable of liquation.

Lead does not appear to form an alloy with silicium; if a solution of silicium in commercial zinc be evaporated, a small globule of lead is always found below the ingot of silicium, and this is never entirely got rid of by heat.—*Comptes Rendus*, August 3, 1857, p. 163.

On the Combinations formed by Glycerine with Muriatic, Hydrobromic, and Acetic Acids. *By* MM. BERTHELOT *and* DE LUCA.

First Part.—Double compounds formed by the union of glycerine with muriatic and hydrobromic acids.

* The fluosilicate of potash may be replaced by a mixture of sand and common salt; but the reduction is less easy.

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Chlorhydrodibromhydrine.. $C^6 H^5 Br^2 Cl = C^6 H^8 O^6 + 2HBr + HCl - 6HO.$

Bromhydrodichlorhydrine.. $C^6 H^5 Cl^2 Br = C^6 H^8 O^6 + 2HCl + HBr - 6HO.$

Trichlorhydrine..... $C^6 H^5 Cl^3 = C^6 H^8 O^6 + 3HCl - 6HO.$

Epidichlorhydrine..... $C^6 H^4 Cl^2 = C^6 H^8 O^6 + 2HCl - 6HO = C^6 H^5 Cl^3 - HCl.$

The regeneration of glycerine with the preceding compounds, which are all free from oxygen and isomeric with the chlorinated and brominated derivatives of a hydrocarbon, is well worthy of notice. It gives rise to some interesting reflections upon the analogies and differences which may exist between the reactions of isomeric compounds.

In fact, last year we published the first example of such a reproduction of glycerine by means of a tribrominated compound analogous to the preceding, and also free from oxygen, tribromhydrine, $C^6 H^5 Br^3$, a body isomeric with bromide of brominated propylene, $C^6 H^5 B . Br^2$. The existence of properties of tribromhydrine, which are exactly conformable with the general theory of the glyceric compounds formulated by one of us, led us to try whether various bodies which present the same composition would be equally capable of becoming converted into glycerine. The following are the results of two experiments made with this object upon two compounds isomeric with tribromhydrine. One of these compounds was discovered within the last four months, and transformed into glycerine by M. Wurtz; the other is the bromide of brominated propylene upon which we have operated.

The compound of M. Wurtz is prepared by treating glycerine with iodide of phosphorus, and acting upon the allyliodic æther produced by bromine; when submitted to the action of silver-salts, it regenerates the glycerine by means of which it was formed.

Notwithstanding the interest presented by this experiment from its analogy with that already perfomed by us upon tribromhydrine, it does not prove the transformation of bromide of brominated propylene into glycerine, which M. Wurtz thought he had realized. In fact, the compound upon which he operated is not identical with the bromide of brominated propylene; it is a new isomer of tribromhydrine, which it resembles in its reactions as also in its origin; we shall call it, for brevity, isotribromhydrine. It is distinguished from bromide of brominated propylene by its physical properties and reactions. Thus isotribromhydrine boils at 422°·6 F., whilst bromide of brominated propylene boils at 377°·6 F., or 45° lower, according to the indications of M. Cahours, who was the first to discover this substance, and verified by ourselves. Tribromhydrine and isotribromhydrine submitted to the action of silver-salts, regenerate glycerine; whilst the same experiment made with bromide of brominated propylene, did not furnish glycerine in appreciable quantities. We operated upon 100 grms. of bromide of brominated propylene (prepared with the propylene resulting from the decomposition of amylic alcohol by heat) and an equivalent proportion of butyrate of silver;

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the whole, mixed with butyric acid and heated for four days to 266° F., furnished as its principal product bibrominated propylene, $C^6 H^4 Br^2$. After a series of treatments arranged in such a manner as not to allow of the escape of any of the glycerine which might have been regenerated, there was obtained only 0·2 gr. of a syrupous, deliquescent extract, charged with saline matters, and which did not appear to present the characters of glycerine.

These results establish an essential difference between the three isomeric compounds, tribromhydrine, isotribromhydrine, and bromide of brominated propylene; the two former, which are derived from glycerine, are capable of reproducing it according to our experiments and the subsequent ones of M. Wurtz; but the bromide of brominated propylene has not hitherto displayed the same property. To establish the conversion of propylene into glycerine, it is not sufficient therefore to operate upon brominated compounds derived from glycerine, but it would be necessary to employ bodies formed with propylene itself, produced for example in the decomposition of amylic alcohol by heat.—*Comptes Rendus*, August 3, 1857, p. 178.

On Huanokine, a New Alkaloid from Peruvian Bark.
By A. Erdmann.

Ten years ago a Peruvian bark was first received at Bremen, which subsequently came into the market as *Cortex Peruvianus* and *Cortex Chinæ regius*, and of which Delondre and Bouchardat have ascertained that it is collected in the north of Lima in the forests of Huanuco, and probably from *Cinchona nitida* ('Quinologie,' Paris, 1854, p. 27).

From 1 pound of bark the author obtained 1 drachm of alkaloid. This differs from all the previously known alkaloids of the Peruvian barks, and the author therefore names it

Huanokine, $C^{20} H^{12} NO$. It has no taste, crystallizes in small, colourless prisms, and has a slight alkaline reaction. The alcoholic solution has a slightly bitter taste. It fuses when heated, and solidifies in a crystalline form; when more strongly heated it sublimes, and in the air the vapour condenses into light, floating flakes. It burns with a smoky flame. It is insoluble in water. At 62°·6 F. it requires 400 parts of alcohol to dissolve it. At a boiling heat it only takes 110 parts. It dissolves in 600 parts of æther at 62°·6 F., and in 470 parts of boiling æther. The sulphate is scarcely soluble in water, but dissolves readily in an excess of acid. The solution is not flourescent. It is difficult of solution in alcohol and æther. It fuses with a yellowish colour. The muriate is readily soluble, and the solution is not fluorescent. It crystallizes in large, clear prisms, and tastes extremely bitter.

The platinum double salt is produced by mixing the solution of the muriate with a solution of bichloride of platinum. It forms a light yellow, crystalline precipitate, which is but sparingly soluble in hot water, alcohol and æther. It is more readily soluble in an excess of solution of bichloride of platinum, and may be obtained

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therefrom in well-developed yellow crystals. Caustic alkalies and alkaline carbonates give a white precipitate with the solutions. Solution of mercury produces a white, insoluble double salt. Perchloride of gold gives a yellow precipitate, and infusion of galls a strong, yellowish-white one. Perchloride of iron, tartrate of antimony, sulphate of copper, iodide of potassium, and oxalate of potash have no action. The analysis made by Dr. Gössmann gave—

C	77·54	77·68	20	77·92
H	7·73	7·76	12	7·79
N	8·81	..	1	9·09
O	..	..	1	5·15

The platinum double salt contained 27·81 and 27·80 per cent. of platinum. According to observations by Dr. Homeier and Dr. Schmidt, this new alkaloid has a very high febrifuge action.—Liebig's *Annalen*, c. p. 341.

On the Precipitation of various Bases by Oxide of Silver. *By* H. Rose.

Oxide of Cobalt.—Towards oxide of cobalt, oxide of silver behaves in the same way as towards protoxides of manganese and iron, except that the action is much slower. If moist oxide of silver be digested with an excess of a solution of sulphate of cobalt, it gradually becomes quite deep black, and converted into a compound consisting of 1 atom of peroxide of cobalt and 1 atom of protoxide of silver. Nevertheless, whether it be prepared at the ordinary temperature or by the aid of heat, and whether it be washed with cold or hot water, it still obstinately retains a certain quantity of insoluble basic sulphate of cobalt.

The compound is not produced by carbonate of silver. If an excess of oxide of silver be employed, the oxide of cobalt is completely thrown down from the solution.

If the black compound be treated, whilst still moist, with muriatic acid, no odour of chlorine is exhibited; but this is evolved distinctly, although not strongly, when it is treated with that acid after being dried. When treated with dilute nitric acid, a powder of the same colour as the compound remains undissolved at first, whilst the acid acquires the colour of a solution of cobalt.

The compound of peroxide of cobalt with protoxide of silver is always of the same composition, even when it is prepared in various ways. It is most easily obtained by mixing solutions of sulphate of cobalt and nitrate of silver, and then adding a little ammonia. There is formed first of all a greenish-blue precipitate, as in a solution of oxide of cobalt by a little ammonia; this however becomes quite black in course of time, and is converted into the compound of peroxide of cobalt and protoxide of silver. This conversion, however, takes place much more slowly than in solutions of the protoxides of iron and manganese under the same circumstances. The tendency of oxide of cobalt to become converted into a higher oxide

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at the cost of the oxide of silver, is far less than that of protoxide of iron, or even of protoxide of manganese.

Oxide of Nickel.—The solution of sulphate of nickel, when treated with oxide of silver, retains its colour, although much oxide of silver is dissolved, and much oxide of nickel precipitated. Oxide of nickel is therefore only partially precipitable by oxide of silver at ordinary temperatures. By boiling, the solution is decolorized, but it does not appear to be possible to precipitate oxide of nickel entirely by oxide of silver.

Oxide of Cadmium.—Although this is one of the weaker bases, it is only partially precipitated from the solution of the sulphate by oxide of silver at ordinary temperatures, and not completely precipitated except by boiling.

Oxide of Zinc.—This is completely precipitated by oxide of silver from the solution of its sulphate, even at ordinary temperatures. By carbonate of silver, oxide of zinc is very imperfectly precipitated at ordinary temperatures, but is entirely thrown down by long boiling.

Between oxide of zinc and oxide of silver there is a certain amount of affinity, but it is difficult to obtain compounds of the two oxides in definite simple proportions. If to a solution of sulphate of zinc so much hydrate of potash be added as to produce complete solution of the oxide of zinc, and then nitrate of silver, so that the fluid separated from the resulting precipitate may still contain oxide of zinc and hydrate of potash, a precipitate is thrown down of a less brown colour than that exhibited by pure oxide of silver. It has however a different composition, according as the solutions are more or less diluted.

Oxide of Lead.—Chloride of lead is completely precipitated from its solution both by oxide and carbonate of silver, but the solutions of nitrate and acetate of lead are only partially precipitated by oxide of silver, but completely by the carbonate.

Between the oxides of lead and silver there is a similar affinity to that between the oxides of zinc and silver. The compound which was long since obtained by Wöhler, may also be obtained in the same way. It is yellow, but readily becomes blackish, and differs in its composition, although always of a yellow colour, according as the one or the other oxide predominates in the solution, and as the dilution is greater or less.

Oxide of Copper.—Perchloride of copper is entirely precipitated by oxide of silver, as is the oxide of copper from solutions of the sulphate and nitrate.

This behaviour may be made use of with great advantage for the preparation of a pure nitrate of silver from silver containing copper. In his memoir, the author gives a detailed description of the process which is to be adopted. This method of separating copper from silver is recommended in preference to most of the known processes by its simplicity.

That the more or less basic nature of the various oxides is dependent both upon the electro-chemical nature of their metals and

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upon the number of atoms of oxygen, the author has attempted to prove on various occasions; this, however, is peculiarly confirmed by the behaviour of copper to silver, and of oxide of copper to oxide of silver. Copper is more electro-positive than silver, and precipitates the latter from its solutions. If oxide of copper and oxide of silver had a similar atomic constitution, oxide of copper would necessarily have stronger basic properties than oxide of silver. But as this is not the case, it follows that the two oxides cannot be similarly composed.

Protoxide of Copper.—By this a gray mass is precipitated from solutions of sulphate and nitrate of silver; this consists of metallic silver and insoluble basic protosulphate and protonitrate of copper; persulphate and pernitrate of copper are dissolved. Protoxide of copper therefore behaves towards solutions of oxide of silver in the same way as a mechanical mixture of equal atomic weights of metallic copper and peroxide of copper would have behaved.

Oxide of Mercury.—Perchloride of mercury is completely precipitated by oxide and carbonate of silver. Pernitrate of mercury with a little oxide of silver gives a white crystalline precipitate of a double pernitrate of silver and mercury. By an excess of oxide of silver, the peroxide of mercury is entirely precipitated. If a solution of persulphate of mercury in dilute sulphuric acid be treated with oxide of silver at ordinary temperatures, the first addition of it causes a separation of basic persulphate of mercury of a yellow colour; by a larger quantity all the peroxide of mercury is thrown down, but the precipitate contains sulphuric acid in the form of a basic salt, which is only completely decomposed by the oxide of silver by long action and repeated stirring. If dry basic persulphate of mercury be treated with moist oxide of silver, it can only be entirely decomposed by boiling.

Protoxide of Mercury.—Protochloride of mercury is decomposed by moist oxide of silver into protochloride of silver and protoxide of mercury; the latter is partially converted into metallic mercury and peroxide of mercury. The protoxide of mercury is precipitated from protonitrate of mercury by oxide of silver.

Perchloride of Gold.—A solution of potassio-chloride of gold is immediately decolorized by moist oxide of silver. The solution contains hydrate of potash, and the insoluble residue consists of the excess of oxide of silver, of chloride of silver, and oxide of gold. With carbonate of silver, carbonate of potash is formed, whilst carbonate of silver, chloride of silver, and oxide of gold remain undissolved. As oxide of gold is insoluble in oxyacids, nitric acid only dissolves oxide of silver from the insoluble residue.

Oxide of Chrome.—From a solution of sulphate of chrome and alumina prepared in the cold, the oxide of chrome is entirely precipitated by oxide of silver. If the solution be mixed at the ordinary temperature with an excess of hydrate of potash, until the oxide of chrome thrown down is again entirely dissolved, and nitrate of silver be then added to this solution in such quantity that a large amount

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of free potash still remains in solution, the precipitate produced consists entirely of oxide of silver. But chromic acid is formed in the solution of oxide of chrome in potash.

Oxide of Bismuth.—Oxide of silver throws down all the oxide of bismuth from a solution of nitrate of bismuth in weak nitric acid. A compound of oxide of bismuth with oxide of silver could not be produced.—*Bericht der Akad. der Wiss. zu Berlin*, 1857, p. 311.

On Lycoresin, Lycostearone and the Bitter Matter of Lycopodium. *By* Dr. Moritz Kamp.

The author has investigated the *Lycopodium Chamæcyparissus* in Boedeker's laboratory. He obtained therefrom,—

1. *The Bitter Matter of Lycopodium*, by first extracting the plant with alcohol, distilling off the alcohol and evaporating. The plant is then extracted with water, and the evaporated extract mixed with that obtained by alcohol. A resin separates. The aqueous solution is precipitated by means of basic acetate of lead, the precipitate is removed, and the excess of the lead salt thrown down by sulphuretted hydrogen. It is then evaporated and extracted with alcohol, which takes up grape-sugar and leaves the bitter matter undissolved. If the latter be now dissolved in water, it is precipitated by basic acetate of lead. The precipitate separated by filtration and washed was suspended in water and decomposed with sulphuretted hydrogen; the filtrate was sufficiently concentrated and left to ferment with yeast until a filtered sample produced no reduction when boiled with Fehling's solution. The filtrate was evaporated to dryness upon the water-bath, and the bitter matter was then dissolved by absolute alcohol. After the alcohol was distilled off and evaporated, the bitter matter remained.

This body crystallizes from a concentrated, syrupous, colourless, aqueous solution in attenuated, pure white needles. It is very soluble in alcohol and æther. It has an extraordinarily intense bitter taste; it is indifferent towards litmus, and contains no nitrogen. Its behaviour towards weak tincture of iodine is peculiarly sensitive and characteristic; the weakest solutions acquire a poppy-red colour therewith, and rather stronger solutions furnish a strong flocculent precipitate of a fine bright brownish-red colour. When boiled with Fehling's solution it effects no reduction, but if it has been previously boiled with sulphuric acid, a strong reduction of Cu^2O takes place. Nitrate of silver gives a white precipitate, which is decomposed, becoming black when boiled. Concentrated sulphuric acid colours the crystals first bright red, and then brown. This bitter matter is therefore probably a still unknown glycoside.

Lycostearone, $C^{30}H^{30}O^4$, is the name given by the author to a body which is obtained from the herb of *Lycopodium Chamæcyparissus*, when this is extracted with alcohol, and the alcohol is distilled off and left to cool. A brownish deposit then separates, which is washed first with alcohol, and then with water. By repeated solution of this mass in boiling alcohol with the addition of animal char-

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coal, and setting the solution, after filtration, to cool, a whitish turbid jelly is at last obtained, which, after washing with cold alcohol, dries into a white, nearly earthy, amorphous, starch-like mass. Even under the microscope no trace of crystallization is discoverable in this; it is inodorous and tasteless, and somewhat fatty to the touch; when heated it begins to fuse between 167° and 169° F., but is only completely melted at 212° F.; when more strongly heated, it becomes brown and evolves an odour resembling that of burning fat; when still more strongly heated, it ignites and burns with a smoky flame. This body is insoluble in cold water; when boiled, a portion is dissolved, which separates again in a gelatinous state on cooling. It is also but slightly soluble in cold alcohol and æther, but dissolves more abundantly when boiled. These solutions are indifferent towards litmus. Both caustic alkalies and alkaline carbonates dissolve it readily and abundantly; acids again separate the dissolved portion. With cold concentrated sulphuric acid it becomes brown, turning black when heated. Analysis:—

C	74·15	30	= 180	74·38
H	12·47	30	30	12·40
O	13·38	4	32	13·22

Lycoresin, $C^{36} H^{32} O^4$, is obtained from the mother-liquors of lycostearone, when they are concentrated and washed after the removal of the alcohol. It remains as a greenish-brown mass. When boiled with a little solution of soda it separates on cooling as a slightly coloured mass, which may be obtained white and crystalline by recrystallization from alcohol.

It is insoluble in water, but abundantly soluble in alcohol and æther. At 338° F. it begins to fuse; when more strongly heated it smells like burning resin, ignites and burns with a smoky flame. It is but slightly soluble in the cold both in pure alkalies and in alkaline carbonates; with the assistance of heat those bodies decompose it. Its alcoholic solution gives no precipitate with alcoholic solutions of nitrate of silver, acetate of baryta, perchloride of copper, and chloride of calcium; it gives a white precipitate with an alcoholic solution of bichloride of mercury. With concentrated sulphuric acid it becomes dark orange, and afterwards brown; on the addition of bichromate of potash to the sulphuric acid, the lycoresin reduces the chromic acid, and a penetrating acid odour is evolved. This body has some resemblance to many resins, such as hartine and Filhol's copal resin. Analysis:—

C	76·98	77·09	36	= 216	77·14
H	11·13	11·33	32	32	11·43
O	11·89	11·58	4	32	11·43

Liebig's *Annalen*, c. p. 298.

On the Preparation of Nitrogenous Bases. *By* Dr. SONNE[illegible]

The author has endeavoured to produce new nitrogen[illegible] by the treatment of the nitrogen compounds of sodium.

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platinum, and palladium with the chlorine compounds of æthyle, formyle, ætherine, benzine, and naphthaline.

Iodide of æthyle and amidochloride of mercury, $HgCl+HgNH^2$ (protochloride of bihydrargyrammonium, $N\left.\begin{matrix}H^2\\Hg^2\end{matrix}\right\}Cl$).—In this experiment 1 part of white precipitate was heated in the water-bath in a sealed tube with 1·5 part of iodide of æthyle, C^4H^5I, as long as a perceptible alteration took place in the substance. The decomposition of 6 ounces of precipitate by 9 ounces of iodide of æthyle required several days, and furnished,—

1. an aqueous solution of low specific gravity;
2. an oleaginous, dark-brown fluid of a higher specific gravity;
3. yellowish crystals.

On opening the tube no evolution of gas took place.

The solution (1) contained perchloride of mercury, muriate of ammonia, and a compound of perchloride of mercury with chloride of æthylammonium, which may be obtained in beautiful crystals.

The solution (2), besides the excess of iodide of æthyle, contained double salts of various æthylized bases, namely iodide of æthylammonium, iodide of diæthylammonium, and iodide of triæthylammonium with perchloride of mercury; all these double salts are readily soluble in alcohol and æther. By water they are decomposed into red iodide of mercury and an oleaginous fluid, which floats upon the surface. The author expelled the bases from this compound by heating it with potash, saturated them with muriatic acid and produced the platinum double salts.

		Platinum.	
The platinochloride of æthylammonium ...	$NC^4H^8Cl+PtCl^2$ gave	39·3	39·5
The platinochloride of diæthylammonium	$NC^8H^{12}Cl+PtCl^2$ ...	35·77	36·0
The platinochloride of triæthylammonium	$NC^{12}H^{16}Cl+PtCl^2$ ...	32·16	32·38

Thus bases are produced by the action of iodide of æthyle upon the nitrogen compound of mercury. In this case, however, it is not a simple decomposition that takes place, but by the mutual action of several equivalents of the two compounds and their decomposition into compounds containing a larger or smaller amount of hydrogen, the four known æthylized bases, which Hofmann prepared by different consecutive operations, are formed at once, with a new one containing mercury. The processes which took place may be represented by the following equation:—

$$6(HgCl+HgNH^2),\ 14(C^4H^5I)=\left.\begin{matrix}NC^{16}H^{20}I\\NC^{16}H^{19}HgI\end{matrix}\right\}7HgI.$$
$$NC^{12}H^{16}I+2HgI.$$
$$NC^8H^{12}I+HgI.$$
$$NC^4H^8Cl+HgCl.$$
$$NH^4Cl,\ 3HCl.$$

The yellowish crystals (3) are purified by washing with hot, absolute alcohol from contamination with the bodies referred to under 1 and 2. These crystals, as the author ascertained with certainty,

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are a compound of periodide of mercury with iodide of tetræthylammonium; their analysis is difficult, but it led to the following numbers:—

Hg	36·11	36·85	34·78	8	=10010·320	36·372
I	49·86	49·12	52·65	9	14273·928	51·864
N	1·58	1·18	1·201	2	350·120	1·272
C	7·983	8·78	8·68	32	2400·000	8·720
H	1·416	1·71	1·79	39	487·500	1·771.

From this we may perhaps deduce the formula $2(NC^{16}H^{20}, I) + 6HgI + Hg^2I$; on boiling with iodide of potassium 1 atom of mercury is separated, which is in favour of the presence of Hg^2I in the compound. Other properties possessed by it, however, are against the admission of the last formula; thus the compound, when it is decomposed as much as possible by sulphuretted hydrogen and boiled with sulphuret of potassium, dissolves completely, which would be impossible if a protosalt (protiodide) of mercury were present.

The behaviour of the yellow crystals also shows that they must contain not only tetræthylammonium, but also another base, which may perhaps be regarded as a tetræthylammonium in which 1 equivalent of H is displaced by Hg. This appeared by the following treatment.

The substance was decomposed by means of oxide of silver, and the alkaline fluid evaporated without any addition. On its surface a fine film of a metallic lustre separated, and this on further evaporation rolled up into scales of crystalline appearance. These gradually settled to the bottom in the form of a black deposit. When the solution was evaporated to dryness, the residue was heated in a flask until it was decomposed, and the gases evolved were conducted into muriatic acid. Triæthylammonium and ætherine were volatilized, whilst carbon and metallic mercury were separated in the flask.

From this behaviour of the substance it follows, that as all the mercury was not precipitated by oxide of mercury, the non-precipitable part, which exactly represents 1 equivalent, is contained in it in an unusual state.

From the behaviour of the alkaline solution evaporated to dryness at a high temperature, it also appears that mercury is contained in it, but also that a nitrogenous base is still present, containing less hydrogen than oxide of tetræthylammonium, which is decomposed at a high temperature into triæthylamine, ætherine, and water (without separation of carbon):—

$$NC^{16}H^{20}O, HO = NC^{12}H^{15}, C^4H^4, 2HO.$$

The black crystalline scales, when heated in a small glass flask, furnish metallic mercury, and deposit carbon with evolution of empyreumatic products.

To determine the nature of this body, the author neutralized the fluid produced from the treatment of the yellow crystals with oxide of silver with muriatic acid. After the small quantity of chloride

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of silver thus separated had been removed, the fluid was evaporated, when tolerably large crystals were deposited. These were separated from the mother-liquor, containing the deliquescent chloride of tetræthylammonium, and purified by recrystallization. In the pure state they form white, shining, right-angled prisms of great stability, which become dim at first in cold water, dissolve when heated, and crystallize again readily. They are also soluble in hot alcohol. When heated in a small glass flask, fine needles are sublimed, with deposition of carbon and metallic mercury, whilst the odour of triæthylamine is evolved. The results of the analysis were as follows:—

Hg	33·96	1	=1251·290	33·25
$NC^{16}H^{20}$	43·32	1	1625·060	43·18
Cl	23·12	2	886·560	23·56

According to this the compound has the composition $NC^{16}H^{20}Cl + HgCl$, and the yellow crystals must consequently contain, besides the periodides of mercury and tetræthylammonium, an organic mercurial compound of the formula $NC^{16}H^{19}Hg$, which may therefore be regarded as tetræthylammonium in which 1 equivalent of hydrogen is displaced by 1 equivalent of mercury, for which reason the author names it hydrargyrotetræthylammonium. The composition of the yellow crystals therefore is,—

$$\left.\begin{matrix} NC^{16}H^{20}, I \\ NC^{16}(H^{19}Hg), I \end{matrix}\right\} + 7HgI.$$

The decomposition of the yellow crystals by oxide of silver is as follows:—

$$\left.\begin{matrix} NC^{16}H^{20}, I \\ NC^{16}(H^{19}Hg), I \end{matrix}\right\} + HgI + 9AgO = \left\{\begin{matrix} 9AgI, 7HgO + \\ + NC^{16}H^{20}O, NC^{16}H^{19}HgO. \end{matrix}\right.$$

If the alkaline fluid, filtered from the oxide of silver, be evaporated to dryness, and then heated until it is decomposed, the following occurs, passing over the well-known decompositions of tetræthylammonium,—

$$4(NC^{16}H^{19}HgO)\,4HO = 4(NC^{12}H^{15}) + 3(C^4H^4), C^4, Hg^4 + 8HO$$

If the alkaline solution be neutralized with muriatic acid, the following takes place:—

$$\left.\begin{matrix} NC^{16}H^{20}O \\ NC^{16}(H^{19}Hg)O \end{matrix}\right\} 3HCl = 2(NC^{16}H^{20}Cl) + HgCl + 2HO.$$

Liebig's *Annalen*, ci. p. 20.

Note on some Properties of Arsenious Acid. *By* M. V. DE LUYNES.

When a mixture of arsenious acid and muriate of ammonia is heated, ammoniacal gas is set free; this is the opposite of what takes place in the action of an acid upon a chloride.

The mixture of the two substances in powder is put into a balloon furnished with an abductive tube, and the temperature is raised. An abundant evolution of ammoniacal gas is produced; it may be

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collected over mercury. In course of time the bubbles of gas appear charged with white fumes, and then the evolution stops.

It appears singular at first that an acid should expel ammonia from its combination. But arsenious acid and muriatic acid in reacting upon each other, furnish water and chloride of arsenic,—

$$AsO^3 + 3HCl = AsCl^3 + 3HO.$$

In the preceding experiment something of the same kind occurs. After the cessation of the evolution of gas a great part of the arsenious acid is found condensed in the upper part of the balloon. This is owing to arsenious acid being more volatile than muriate of ammonia. This difference of volatility prevents the two substances from being kept in contact during a tolerably long time, and necessarily abridges the period of evolution of gas, but this is not the sole cause of its cessation. On opening the balloon after cooling, white fumes, analogous to those furnished by chloride of arsenic, escape; they strongly redden litmus-paper. On treating the solid residue with water, the white vapours disappear, and a liquid is obtained which reacts upon tincture of litmus in the manner of the strong acids. This action is due to the muriatic acid produced from the chloride of arsenic by decomposition with water. Thus, during the first part of the reaction, the ammonia is eliminated in consequence of the affinity of the arsenious acid for muriatic acid; chloride and perhaps oxychloride of arsenic is formed. The proportion of the latter compound becoming more considerable, an inverse reaction is produced, which opposes the continuance of the evolution. Arsenious acid therefore acts upon muriate of ammonia in the manner of a metallic oxide; ammonia is set free, and a chloride and water are produced.—*Comptes Rendus*, June 29, 1857, p. 1354.

On Compounds of Nitrate of Silver with Iodide of Silver.
By Albert Kremer.

By heating a concentrated solution of nitrate of silver with iodide of silver, a white crystalline compound, $AgI + AgO, NO^5$, is obtained. It fuses at 201° F. (This compound has already been obtained by Schnauss.)

		Calculated.
Iodide of silver.....	58·10	58·05
Nitrate of silver	42·20	41·95

During fusion the body dissolves an excess of iodide of silver, acquires a yellow colour, and a lower melting-point.

The author also obtained another crystalline compound, the analysis of which gave—

Iodide of silver.....	2·82	2·72
Nitrate of silver	97·33	

Analogous compounds of bromide of silver could not be obtained in the humid way, any more than the crystalline compound, $AgI + 2(AgO, NO^5)$, described by Weltzien.—*Journ. für Prakt. Chemie*, lxxi. p. 54.

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On Chlorostyrole. By W. KUBEL.

Protochloride of styrole, $C^{16} H^8 Cl^2$, was prepared by passing dry chlorine gas into dry styrole; if it be heated with alcoholic solution of potash, a heavy oil of a pleasant odour is produced, which strongly irritates the eyes, producing tears. This latter compound is decomposed during distillation with a strong evolution of muriatic acid, but it may be distilled colourless with aqueous vapour; a determination of the chlorine furnished 18·58 per cent. of chlorine, whilst chlorostyrole, $C^{16} H^7 Cl$, contains 25·58 per cent.

If this oil with a little water poured over it be left standing in the air, the water soon acquires a strong acid reaction from free muriatic acid, and laminar crystals separate; the crystals were pressed between bibulous paper, and purified by sublimation. All their properties indicated benzoic acid, with which the found composition agreed.

	Calculated.		Found.
C	68·85	14	68·32
H	4·92	6	4·87
O	26·23	4	

Liebig's *Annalen*, cii. p. 238.

ANALYTICAL CHEMISTRY.

On the Separation of Iron from Manganese. *By* FREDERICK FIELD, M.R.I.A., F.C.S.*

WHEN a persalt of iron is digested with oxide or carbonate of lead at a moderate temperature, the whole of the iron is precipitated; the decomposition takes place more rapidly upon the application of heat. There is no decomposition in solutions of the protosalts of manganese when similarly treated. By boiling the solution, obtained by the action of the hydrochloric acid upon commercial oxide of manganese, with oxide of lead (litharge will answer every purpose), the liquid becomes colourless after a few minutes, and a basic salt of iron is precipitated. It is, however, necessary to separate the lead from the manganese, which is best effected by the addition of a slight excess of sulphate of soda before filtration, and a small quantity of sulphuretted hydrogen-water (or the gas) to the filtrate. It is almost impossible to separate all the lead by means of sulphuric acid or a soluble sulphate. The following experiments will show the accuracy of the method.

1. 10·00 grs. manganaso-manganic oxide, $Mn^3 O^4$, prepared from the carbonate, were dissolved with 10·00 grs. pure metallic iron in dilute nitro-hydrochloric acid.

2. 10·00 grs. manganoso-manganic oxide were treated in the same manner with 1·00 gr. iron.

3. 10·00 grs. iron and 1·00 gr. manganoso-manganic oxide were employed.

* Communicated by the Author.

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When the substances were dissolved and the iron completely peroxidized, the solutions were evaporated to expel any great excess of acid, and severally boiled with about 100 grs. of litharge. After cooling, a solution of sulphate of soda was added in excess, the liquids filtered off, and the precipitates thoroughly washed.

A slight stream of hydrosulphuric acid was passed through each, which occasioned a small precipitate of sulphide of lead. On refiltration, and boiling to expel excess of hydrosulphuric acid, the manganese was precipitated by carbonate of soda, and after washing and desiccation, heated to redness for its conversion into manganoso-manganic oxide.

		Taken.
1. yielded	9·94 $Mn^3 O^4$	10·00
2. „	9·96 „ „	10·00
3. „	0·97 „ „	1·00

The oxide was perfectly pure. The carbonates of the alkalies precipitated snow-white carbonate of manganese. Sulphide of ammonium, pure flesh-coloured sulphide, with no tinge of black, and ferrocyanide of potassium gave no shade of blue. Equally satisfactory results were obtained in the estimation of the iron.

The employment of hydrosulphuric acid is indispensable in the process. When perchloride of iron and oxide of lead are boiled with weak hydrochloric acid, no precipitate is produced upon the addition of sulphuric acid or sulphate of soda. On cooling, large crystals of chloride of lead are produced, and on further concentration more of the salt may be obtained. It appears that no sulphate of lead is formed. When persulphate of iron and chloride of lead are boiled with hydrochloric acid (the latter even in minute quantities), the whole is dissolved, and chloride of lead separates on cooling.

The introduction of a third metal for the separation of the two already existing, may be urged against the above process; but it must be recollected, that to obtain pure oxide of manganese from the commercial oxide, it is always necessary to pass a stream of sulphuretted hydrogen through the acid liquid to precipitate traces of copper, &c. which generally exist in the mineral. In the method under consideration, the sulphuretted hydrogen is merely added *after* the separation of the iron instead of *before*; any traces of copper, &c. being separated with the small quantity of lead which has escaped precipitation by sulphuric acid.

PROCEEDINGS OF SOCIETIES.

Royal Society.

June 18, 1857. (The Lord Wrottesley, President, in the Chair.)

"Researches on the Phosphorus-Bases." By Dr. Hofmann and A. Cahours.

In a note on the action of chloride of methyle upon phosphide of calcium, communicated more than ten years ago to the Institute of France, M. Paul Thénard pointed out the existence of a series of

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bodies which correspond to the compounds of phosphorus with hydrogen, which may, in fact, be viewed as phosphoretted hydrogens, the hydrogen of which is replaced by an equivalent quantity of methyle.

It is now many years since M. Paul Thénard abandoned the study of the phosphorus-compounds, for the first knowledge of which we are indebted to him. The unfinished state in which these researches remained, and the rich and abundant harvest collected since that period, in all the neighbouring fields of science, necessitated a revision of the subject. The discovery of methylamine, dimethylamine, and trimethylamine, and of the corresponding terms in the ethyle- and amyle-series, had shown that the hydrogen in ammonia may be replaced by binary molecules, such as methyle, ethyle, amyle and phenyle, the newly-formed compounds retaining the basic character of the original ammonia molecule; whilst the production of triethylestibine and triethylarsine had furnished the proof that the total replacement of the hydrogen in the indifferent antimonietted and arsenietted hydrogens exalts the chemical character of these compounds in a most remarkable manner, the methylated and ethylated bodies exhibiting basic characters scarcely inferior to those of ammonia itself. It remained, therefore, to be investigated whether phosphorus, which by its chemical tendencies stands between nitrogen and arsenic, would exhibit a similar deportment. It had to be ascertained in what manner the gradual entrance of binary molecules in the place of the hydrogen in phosphoretted hydrogen would change the character of the original compound. Again, the discovery of the tetrethylated ammonium-bases had opened a new field of research, in which the corresponding terms of the antimony- and arsenic-series were rapidly brought to light. It was indeed possible to predict with certainty, that an appropriately selected method would lead to the production of the analogous derivatives of phosphoretted hydrogen. The time for resuming the study of the phosphorus-bases had in fact arrived.

We have been engaged for a considerable time in the investigation of this subject, and now beg to offer to the Royal Society in the following pages a short abstract of our results.

In the first place, we have endeavoured to obtain the bases corresponding to phosphoretted hydrogen, by a method analogous to that followed by M. Paul Thénard, simply substituting for the chloride of methyle the iodide, and for the phosphide of calcium the more energetic phosphide of sodium. After many unsuccessful experiments, however, we were compelled to abandon this plan, which is quite uncertain, unproductive, and highly dangerous.

The question then resolved itself into the discovery of a method which would yield us the desired substances conveniently, without danger, in considerable quantity, and in a state of absolute purity.

It appeared that the action of terchloride of phosphorus on zinc-methyle, zinc-ethyle, &c., the remarkable substances discovered by Dr. Frankland some years ago, would enable us to attain the contemplated result. Experiment has fully confirmed this anticipation.

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The bases Me_3P and E_3P, the products of this reaction, which we propose to call respectively *trimethylphosphine* and *triethylphosphine*, remain united with chloride of zinc, and a simple dilution with an alkali is all that is necessary to liberate them.

$$3ZnCl, Me_3P + 6KO = 3KCl + 3KO, ZnO + Me_3P$$

$$3ZnCl, E_3P + 6KO = 3KCl + 3KO, ZnO + E_3P$$

They are obtained in this way as volatile oils, of a peculiar and strongly marked odour, and possessing distinctly basic properties.

We limit ourselves in this abstract to giving a synoptical table of the several compounds which have been the subject of our researches, the preparation and properties of which, together with the analytical details, are fully given in the complete paper which accompanies this note.

Methyle-series.

Trimethylphosphine	Me_3P
Platinochloride of trimethylphosphine.	$Me_3P, HCl, PtCl_2$
Binoxide of trimethylphosphine.....	Me_3PO_2
Bisulphide of ditto	Me_3PS_2
Biselenide of ditto	Me_3PSe_2
Iodide of phosphomethylium.....	Me_4PI
Platinochloride of ditto	$Me_4PCl, PtCl_2$
Aurochloride of ditto	$Me_4PCl, AuCl_3$
Iodide of phosph'ethyltrimethylium ..	$(Me_3E)PI$
Platinochloride of ditto ..	$(Me_3E)PCl, PtCl_2$
Iodide of phosph'amyltrimethylium ..	$(Me_3Ayl)PI$
Platinochloride of ditto ..	$(Me_3Ayl)PCl, PCl_2$

Ethyle-series.

Triethylphosphine.....	E_3P
Platinochloride of triethylphosphine..	$E_3P, HCl, PtCl_2$
Binoxide of ditto ..	E_3PO_2
Bisulphide of triethylphosphine	E_3PS_2
Biselenide of ditto	E_3PSe_2
Iodide of phosphethylium.....	E_4PI
Platinochloride of ditto	$E_4PCl, PtCl_2$
Aurochloride of ditto	$E_4PCl, AuCl_3$
Iodide of phosphomethyl-triethylium .	$(MeE_3)PI$
Platinochloride of ditto ..	$(MeE_3)PCl, PtCl_2$
Iodide of phosph'amyltriethylium....	$(AylE_3)PI$
Platinochloride of ditto	$(AylE_3)PCl, PtCl_2$

On glancing at the phosphorus-compounds noticed in the preceding abstract, a comparison of these substances with the corresponding terms of the nitrogen-, arsenic-, and antimony-series is unavoidably forced upon us. Whether we consider the composition, or whether we review the properties of these groups, the most striking analogies, indeed an almost perfect parallelism, cannot be mistaken; similar formulæ, similar modes of combination, similar decompositions.

This analogy is particularly manifest in the compounds belonging

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to the *ammonium-type*. In these remarkable bodies, nitrogen, phosphorus, arsenic, and antimony appear to play absolutely the same part. It is more especially in the oxides of these compound metals that the analogy of composition induces a perfect identity of properties, and, indeed, of very salient properties, which may be traced in almost every direction. If we were satisfied with the study of the reactions of these bodies, we should never suspect, in compounds possessing such a close similarity of properties, the presence of elements so dissimilar as nitrogen, phosphorus, arsenic, and antimony; they might, moreover, be confounded with potassa and soda, by which they are scarcely surpassed in alkaline power.

Only the deportment of the hydrated oxides, under the influence of heat, distinguishes the derivatives of nitrogen from the corresponding terms of the phosphorus-, arsenic-, and antimony-series.

If we regard, on the other hand, the compounds belonging to the *ammonia-type*, we observe that the electro-positive character of the substances gradually rises in intensity from the nitrogen- to the antimony-compounds. Thus, trimethylamine and triethylamine are not capable of uniting with oxygen, chlorine, bromine, and iodine; a power which the corresponding terms of the phosphorus-, arsenic-, and antimony-series possess in a high degree.

Triethylamine unites with the acids, producing compounds of the ammonium-type, and containing

$$E_3N, HCl$$
$$E_3N, HSO_4$$
$$E_3N, HNO_6$$

The corresponding compounds in the arsenic- and antimony-series do not exist; at all events chemists have not yet succeeded in preparing them. Triethylarsine and triethylstibine combine only directly with oxygen, chlorine, sulphur, &c., producing saline bodies which have the composition respectively,—

E_3AsO_2	E_3SbO_2
E_3AsCl_2	E_3SbCl_2
E_3AsS_2	E_3SbS_2

In the phosphorus-series, lastly, the two classes are represented. Triethylphosphine not only forms compounds analogous to the salts of triethylamine, but also the terms corresponding to the binoxides of triethylarsine and triethylstibine. We have in the first place the terms

$$E_3P, HCl$$
$$E_3P, HSO_4$$
$$E_3P, HNO_6,$$

and in the second place compounds of the formula

$$E_3PO_2$$
$$E_3PCl_2$$
$$E_3PS_2$$

The phosphorus-compounds accordingly hold a position intermediate between the nitrogen-compounds on the one hand, and the

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arsenic- and antimony-series on the other. It cannot, however, be denied that the phosphorus-bodies exhibit rather a tendency towards the arsenic- and antimony-series, than towards the nitrogen-group.

This cannot surprise us, when we consider the close analogies which phosphorus and arsenic present in many other directions. Both phosphorus and arsenic form well-characterized polybasic acids; the acids of antimony are not yet sufficiently investigated, but the acids of nitrogen, which are better examined, are all found to be monobasic. The equivalent numbers, too, of phosphorus, arsenic, and antimony, present a remarkable connexion, the difference between those of phosphorus and arsenic, and those of arsenic and antimony being virtually the same—

Phosphorus.....	31	} difference 44,
Arsenic	75	
Antimony	120	} difference 45,

whilst the equivalent of nitrogen stands altogether apart from the rest.

The same relative position of the elements nitrogen, phosphorus, arsenic, and antimony, may also be traced in their hydrides,

$$H_3N \quad H_3P \quad H_3As \quad H_3Sb.$$

Ammonia is a powerful alkali; phosphoretted hydrogen unites only with hydrobromic and hydriodic acids, whilst in arsenietted and antimonietted hydrogen, the power of combining with acids has altogether disappeared. In these hydrogen-compounds the gradation of properties is indeed even more marked than in their trimethylated and triethylated derivatives. On comparing the terminal points of the series, ammonia and antimonietted hydrogen, we cannot fail to be struck by the dissimilarity of properties which at the first glance appears to limit the analogy of the two compounds to a mere parallelism of composition.

In the methylated and ethylated derivatives of these compounds, the intensity of the chemical tendencies in general is so much raised, that the gradation is no longer perceptible to the same extent.

British Association for the Advancement of Science.—Meeting held at Dublin, September 1st, 1857.

Preliminary Notice of Researches on the Assimilation of Nitrogen by Plants. *By* Messrs. Lawes, Gilbert, *and* Pugh.

The great importance of settling the question, whether or not plants can assimilate the free nitrogen, of which the atmosphere to such a great extent consists, was first illustrated. In a purely scientific point of view, the question was of high interest; and if answered in the affirmative, this would add a striking fact to the history both

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of nitrogen itself and of the vegetative functions. A true theory of many agricultural facts and practices also required a definitive solution of this debated point. The earlier writers supposed that the free nitrogen of the air could be taken up by plants. De Saussure and others came to an opposite conclusion; and this latter view had been pretty generally adopted by scientific observers. M. Boussingault in particular, had adduced experimental evidence to show that plants did not assimilate the free nitrogen of the air. But during the last few years an extensive and elaborate series of investigations had been made by M. G. Ville of Paris, the results of which led him to conclude, that plants sometimes assimilated a considerable amount of free nitrogen. M. Boussingault had followed up the inquiry in various ways, and still maintained the opposite opinion. It was hence highly desirable that others should undertake the subject; and it was the plan adopted by the authors to this end, and the indications so far obtained, that they now brought before the Section. They described the several methods adopted by M. Boussingault and M. Ville respectively, and then illustrated by drawings their own methods and progress. In all cases their plants grew, in the first instance, in soil and atmosphere destitute of all combined nitrogen except that contained in the seed sown. To some, however, as their growth seemed to indicate the need, for the sake of comparison, small and known quantities of ammonia were supplied. Drawings of the progress of the plants showed a very considerable increase of growth where this ammoniacal supply was given. In some of these cases, the plants promised to yield seed, and their height and general development was pretty natural. In other instances, where only the combined nitrogen of the seed sown, and the free nitrogen of the air were available, the plants remained exceedingly small, and withered before coming to perfection. The quantitative result could not, however, be known until the growing plants, the soil, and the pots in which they grew, were analysed;—when the debtor and creditor account, so to speak, of the nitrogen could be made up. Collateral researches were briefly described, the object of which was to throw light on the relation of the gases evolved during the growth of plants to constituents actually assimilated; and also others, to show whether free nitrogen was a product of the decomposition of organic matters under certain circumstances. A discussion followed in which the President and Professor Daubeny took part. The latter gentleman expressed his satisfaction that the question of the assimilation of free nitrogen by plants was now taken up, and was being investigated on such a considerable scale at Mr. Lawes' Laboratory; for he had read, with some surprise, the apparent sanction given by a Commission of the Academy of Sciences of France to the opinions of M. Ville, which so many scientific considerations would lead us to hesitate in adopting. After further remarks from Dr. Gilbert, Dr. Pugh entered into some fuller explanations illustrating the methods adopted, and the difficulties and sources of error to be overcome or avoided.—*Communicated by the Authors.*

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THE CHEMICAL GAZETTE.

No. CCCLX.—October 15, 1857.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Constitution of Fulminating Mercury. *By* A. KEKULÉ.

WITH regard to the nature of fulminating mercury and fulminating silver, Gerhardt long since expressed the opinion that these bodies were nitro-products containing NO^4, and consequently shared their principal properties with those explosive organic bodies which we call nitro-compounds. The author suspected that the constitution might be such that the half of the nitrogen was contained in them as NO^4, and the other half in combination with the half of the carbon as cyanogen; fulminating mercury would then be—

$$C^2(NO^4)(C^2N)Hg^2,$$

and in its composition it would have the greatest analogy with a large number of known bodies, amongst others, for example, chloroform:—

$$C^2HClClCl.$$

It might be regarded as nitrited chloroform, in which the chlorine is replaced partly by cyanogen and partly by mercury.

The following compounds may be referred to the same type:—

C^2	H	H	H	H	Marsh-gas.
C^2	H	H	H	Cl	Chloromethyle, &c.
C^2	H	Cl	Cl	Cl	Chloroform.
C^2	(NO^4)	Cl	Cl	Cl	Chloropicrine.
C^2	(NO^4)	(NO^4)	Cl	Cl	Marignac's oil.
C^2	(NO^4)	Br	Br	Br	Bromopicrine.
C^2	H	H	H	(C^2N)	Acetonitrile.
C^2	Cl	Cl	Cl	(C^2N)	Trichloracetonitrile.
C^2	(NO^4)	Hg	Hg	(C^2N)	Fulminating mercury.
C^2	(NO^4)	H	H	(C^2N)	Hypothetical fulminic acid.

Fulminating mercury approaches most closely to chloropicrine and acetonitrile. Like the former it is a nitro-compound, and like acetonitrile (cyanide of methyle) a cyanogen compound. It might be regarded as nitrited acetonitrile, of which the two atoms of hydrogen are replaced by mercury, so that the hypothetical fulminic acid would be nothing but nitroacetonitrile.

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Taking such a view of the nature of fulminating mercury, it became interesting to study its behaviour with chlorine, as it was to be anticipated that by the action of chlorine upon fulminating mercury both the cyanogen and the mercury would be removed and replaced by chlorine, and that thus chloropicrine would be formed together with chloride of mercury and chloride of cyanogen.

The author's experiments convinced him that the decomposition of fulminating mercury by chlorine takes place in accordance with the following equation:—

$$C^2(NO^4\,Cy)\,Hg^2 + 3Cl^2 = C^2(NO^4)\,Cl^3 + Cy\,Cl + 2HgCl,$$

but that the chloropicrine formed is mixed on the one hand with chloride of carbon, and on the other with the bodies containing cyanogen, which are produced, according to Serullas and Bouis, during the action of chlorine upon moist cyanogen gas (chlorcyanole).

That chloropicrine is actually formed by this action of chlorine upon fulminating mercury, appears to be proved by the fact that in the distillation of fulminating mercury with chloride of lime, chloropicrine may be easily obtained in a state of perfect purity.

If fulminating mercury be decomposed by an excess of sulphuretted hydrogen, a fluid is obtained, which is perfectly neutral after the volatilization of the excess of the reagent, and contains sulphocyanide of ammonium. But that only one-half of the carbon of the fulminating mercury is contained in this cyanide, is apparent from a determination of the sulphur in the sulphuretted acid formed by Liebig and Gay-Lussac, as these chemists obtained 1·86 grm. of sulphate of baryta from 2·268 grms. of fulminating mercury, whilst 3·70 ought to have been obtained, if all the carbon had been transferred into the sulphocyanide. The author has also found, that in the decomposition of fulminating silver or fulminating mercury by sulphuretted hydrogen or soluble metallic sulphurets, carbonic acid is set free; this appears to have been hitherto overlooked, but the author regards it as an essential product of the decomposition.

The formation of Schischkoff's isocyanuric acid may be very well explained by the author's view of the nature of fulminic acid, if we suppose that two molecules of fulminic acid unite with reception of water and elimination of carbonic acid and ammonia (perhaps by the nitro-group of one molecule undergoing and inducing decomposition):—

$$2C^2(NO^4)\,Cy\,H^2 + H^2O^2 = C^2(NO^4)\,Cy^2H^3O^6 + C^2O^4 + NH^3.$$

The formation of fulminating mercury from nitric acid and alcohol in the presence of mercury appears to be similar to that of chloroform from alcohol when oxidizing and chloridizing substances act simultaneously. In the same way fulminating mercury is produced when besides oxidation (by nitric acid) the conditions exist (which may be set up by cyanogen and mercury) which the chlorine exhibits in chloroform, whilst at the same time the strong nitric acid has a nitrogenizing action.

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This theory of the formation of fulminating mercury acquires some probability by the following mode of formation of chloropicrine. When a mixture of strong nitric acid and alcohol (such as is used for the preparation of fulminating mercury) is mixed with chloride of sodium instead of the mercurial salt, heat is produced in a few minutes, the mass begins to boil of itself, and a fluid distils over, from which the addition of water separates a heavy oil, which has exactly the characteristic odour of chloropicrine. This mode of formation of chloropicrine has a further interest, because it has hitherto been prepared only from nitro-compounds, and indeed from none which contain less than 12 atoms of carbon.—Liebig's *Annalen*, ci. p. 200.

Researches on the Ammonia-cobalt Bases.

By WOLCOTT GIBBS *and* F. A. GENTH.

[Continued from page 275.]

Xanthocobalt.

The salts of xanthocobalt may be prepared by two distinct processes, either directly from ammoniacal solutions of salts of cobalt, or from neutral, acid, or ammoniacal solutions of the salts of roseocobalt or purpureocobalt. In any case, the gas arising from the action of nitric acid upon starch or sawdust, and which may be considered as a mixture of CO^2, NO^2, NO^3, and NO^4—the last probably in excess—is to be passed into the solution. A more or less rapid absorption, accompanied by copious fumes of carbonate of ammonia, takes place. The colour of the liquid gradually changes to a dark reddish-brown or dark sherry-wine colour, and the liquid on cooling generally deposits an abundance of a salt of xanthocobalt in brown-yellow crystals. When a current of the red gas above mentioned, and which we shall denote by the symbol NO^x, is passed into an acid solution of cobalt and ammonia, an absorption also usually takes place, but in this case no xanthocobalt is produced, but only a beautiful yellow crystalline salt, which is the ammonia nitrite of cobalt, corresponding to the yellow potash salt, first described by Fischer*, some years afterwards re-discovered and analysed by St. Evre†, and finally examined by Stromeyer‡. The formation of this compound is easily prevented, by keeping the solution ammoniacal by constant additions of ammonia§.

The salts of xanthocobalt have a dark sherry-wine or brown-yellow colour. They are rather more soluble, both in hot and cold water,

* Pogg. Ann., lxxiv. 115, and lxxxviii. 496.

† Compt. Rend., xxxiv. 479, and Ann. de Chimie et de Physique, xxxviii. 177.

‡ Journ. für Prakt. Chemie, lxi. 41; and Chemical Gazette, vol. xiv. p. 113.

* The employment of the double nitrite of cobalt and potash as a means of separating cobalt from other metals was first suggested by Fischer and afterwards by St. Evre and Stromeyer. As the salt is insoluble in a solution of acetate of potash and in alcohol, it is easy to wash it completely, but after washing it is difficult to estimate the cobalt accurately by drying and weighing upon a filter. We have found that a very satisfactory result may be obtained by weighing the

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than the salts of roseocobalt, purpureocobalt, or luteocobalt; the solutions when dilute have a yellow colour; when concentrated, they are dark-brown yellow. Solutions of these salts are decomposed by boiling, though sometimes with difficulty; in some cases, however, a temperature much below the boiling-point produces an incipient decomposition after a short time, so that great care must be taken in evaporating for the purpose of crystallization. During the decomposition by boiling, ammonia is given off, while a heavy black or dark-brown powder is thrown down. The addition of a mineral acid prevents the decomposition, but produces, even when in very small quantity, a chemical change of a different kind, deutoxide of nitrogen being given off, while a salt of purpureocobalt is formed, which remains mixed with the undecomposed salt of xanthocobalt, and which it is difficult to separate. A few drops of acetic acid, however, added to a solution of a salt of xanthocobalt, so as to produce a slightly acid reaction, will usually suffice to prevent decomposition, if the solution be evaporated at a gentle heat. The dry salts of xanthocobalt heated in a porcelain crucible are easily decomposed, with copious evolution of red vapours, and afterwards of ammonia, while a black powder remains. We have not been able to detect any new ammonia-cobalt bases among the products of the decomposition of solutions of these salts, by simple boiling or heating in the dry way.

Xanthocobalt differs from the other ammonia-cobalt bases by containing deutoxide of nitrogen as a couplet in addition to ammonia. Considering it as a primary radical, we attribute to it the formula $NO^2 . 5NH^3 . Co^2$, and it is evident that it differs from roseocobalt and purpureocobalt only by one equivalent of deutoxide of nitrogen. The passage of the salts of these two bases into salts of xanthocobalt by the simple absorption of NO^2 is thus easily explained, as is the decomposition of the salts of xanthocobalt into NO^2 and salts of purpureocobalt.

It is, however, proper to remark, that, inasmuch as the salts of xanthocobalt which we have examined in all cases appear to con-

cobalt in the form of mixed sulphates of cobalt and potash. According to Stromeyer, Fischer's salt has the formula

$$Co^2O^3 . 2NO^3 + 3KO, NO^3 + 2HO.$$

When this is heated with sulphuric acid till the excess of acid is expelled, there remains a mixture of sulphates having the formula

$$2CoO, SO^3 + 3KO, SO^3.$$

We therefore dry the salt carefully, burn the filter upon the cover of a deep platinum crucible, and bring the ashes and salt into the crucible itself. A few drops of sulphuric acid are then added, so as to cover the mass, and the whole is then treated precisely as we described on page 144, though in this case a higher heat is to be used. From the weight of the mixed sulphates the quantity of cobalt is easily calculated. This method gives very acurate results, because the cobalt forms only about 14 per cent. of the substance weighed. In an experiment made to test the accuracy of Stromeyer's formula,

0·6671 gr. gave 0·6437 gr. mixed sulphates of cobalt and potash = 13·66 per cent. cobalt.

The formula requires 13·63 per cent.

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tain water in the proportion of at least one equivalent. It is possible that the view we have taken of their constitution may not be precisely accurate, and that they may contain NO^3 as a couplet in place of NO^2. This will be evident from a simple inspection of the formulæ of the chloride, nitrate, and sulphate of xanthocobalt, which are, as we write them at present,—

$$NO^2 . 5NH^3 . Co^2 O, Cl^2 + HO.$$
$$NO^2 . 5NH^3 . Co^2 O^3, 2NO^5 + HO.$$
$$NO^2 . 5NH^3 . Co^2 O^3, 2SO^3 + HO.$$

No chemical analyses could, probably, in substances of such high equivalents, enable us to say with certainty that there may not be in these formulæ an equivalent of hydrogen too much. In this case the three formulæ would read—

$$NO^3 . 5NH^3 . Co^2 O, Cl^2.$$
$$NO^3 . 5NH^3 . Co^2 O^3, 2NO^5.$$
$$NO^3 . 5NH^3 . Co^2 O^3, 2SO^3.$$

The difficulty of analysing these salts must also be fairly considered in forming an opinion as to their constitution. We adopt provisionally the formula first given, in the hope that a more extended study of the products of decomposition will enable us hereafter to fix the constitution with certainty. In the mean time, we will only remark, that the analyses of the nitrate of xanthocobalt, which is of all salts of the base the easiest to prepare in a state of absolute purity, correspond exactly to the formula

$$NO^2 . 5NH^3 . Co^2 O^3, 2NO^5 + HO.$$

Chloride of Xanthocobalt can be most readily prepared by decomposing a solution of the sulphate by chloride of barium. After separation of the sulphate of baryta by filtration, a few drops of acetic acid may be added to the filtrate, which, after evaporation by a gentle heat, will yield on standing large crystals of the chloride. This process is in fact the only one by which we have been able as yet to prepare this salt.

The chloride of xanthocobalt cannot be prepared by the direct action of a current of NO^x upon an ammoniacal solution of the chloride of cobalt. It is true that in this case an abundance of a brown-yellow crystalline salt is obtained, which might easily be mistaken for the chloride. The salt is, however, a mixture of a large quantity of the nitrate of xanthocobalt with a much smaller quantity of another salt, which appears to be the chloride of a distinct base, but which is not yet fully studied.

The equation which represents the formation of the chloride of xanthocobalt by double decomposition, is simply

$$NO^2 . 5NH^3 . Co^2 O^3, 2SO^3 + 2BaCl = 2BaO, SO^3 + NO^2 . 5NH^3 . CO^2 O, Cl^2.$$

The chloride of xanthocobalt crystallizes in brown-yellow crystals, which, when large, have a faint reddish tinge. They are usually very well defined, and exhibit a beautiful iridescence upon their

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surfaces, but we cannot at present describe their form. The salt is quite soluble in hot water, but the solution is easily, though only partially, decomposed at a boiling heat, and even, when quite neutral, at a lower temperature. On boiling, ammonia is evolved in abundance, while a heavy black precipitate is thrown down; it requires very long boiling to produce a complete decomposition. The salt is rather insoluble in cold water; hydrochloric acid precipitates it unchanged in the cold, and the same effect is produced by the solutions of the alkaline chlorides. Acids, even when dilute, easily and completely decompose the chloride of xanthocobalt by boiling. Hydrochloric acid in large excess, by long boiling, converts the salt completely into chloride of purpureocobalt, deutoxide of nitrogen, and occasionally chlorine, being given off. Sulphuric and nitric acid also decompose the chloride, but with these acids the decomposition generally goes so far as to produce salts of cobalt, or double salts of cobalt and ammonia. Oxalic acid also produces complete decomposition by long boiling, oxalate of cobalt and oxalate of ammonia being formed. Even strong acetic acid produces, on boiling with the salt, a partial decomposition. Alkalies readily decompose a solution of the chloride when heated, ammonia being evolved, while a black powder is thrown down. The dry chloride is easily decomposed below a red heat. An abundance of red vapours is at first given off, afterwards ammonia is evolved, and finally a black superoxide of cobalt remains.

Reducing agents, in certain cases, completely decompose the solution of the chloride of xanthocobalt, giving salts of cobalt and ammonium. Thus a current of sulphydric acid gas passed for some time through the solution gives a precipitate of sulphur and sulphide of cobalt, while nitrogen gas escapes, and chloride and sulphide of ammonium remain in solution. The decomposition is similar in an acid solution, but of course no sulphide of cobalt is precipitated.

We made this experiment in the hope of decomposing the NO^2 in the chloride in a manner similar to the well-known reaction in the case of organic compounds containing NO^4. For the same reason we also boiled the chloride with acetic acid and iron filings, in the hope of obtaining a reaction analogous to that which is produced under the same circumstances with nitrobenzol, nitronaphthaline, &c., as observed by Béchamp. The experiments, however, led to no interesting result.

Chloride of xanthocobalt has the formula $NO^2 . 5NH^3 . Co^2O, Cl^2 + HO$, which requires—

	Equivs.		Calculated.	Mean.	Found.	
Cobalt	2	59	22·52	22·32	22·34	22·29
Chlorine ..	2	71	27·09	27·08	26·94	27·22
Hydrogen ..	16	16	6·10	6·17	6·18	6·16
Nitrogen ..	6	84	32·06	31·90	31·84	31·97
Oxygen	4	32	12·23	12·53		

Chloroaurate of Xanthocobalt.—This salt is readily formed by adding a solution of terchloride of gold to one of the chloride of

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xanthocobalt. Beautiful yellow needles are thrown down, which may easily be purified by re-solution in hot water and crystallization. The chloroaurate of xanthocobalt crystallizes in beautiful brown-yellow iridescent prisms, which belong to the trimetric or right rhombic system, according to Prof. Dana's measurements.

The formula of this salt is $NO^2 . 5NH^3 . Co^2O, Cl^3 + AuCl^3 + 2HO$, which requires—

	Equivs.	Calculated.	Found.
Cobalt	2	10·26	10·28
Gold.....	1	34·28	34·18
Chlorine	5	30·89	31·12

Chloroplatinate of Xanthocobalt.—This salt is easily prepared by direct combination. It has a fine orange-yellow colour, and is with difficulty soluble both in hot and cold water, but it may be re-crystallized from a hot solution in dilute hydrochloric acid. It is represented by the formula $NO^2 . 5NH^3 . Co^2O, Cl^3 + 2PtCl^2 + 2HO$, which requires—

	Equivs.	Calculated.	Found.
Cobalt	2	9·52	9·45
Platinum	2	31·87	32·02

The analysis was made in this case by gently igniting the salt in a platinum crucible, and afterwards dissolving out the chloride of cobalt by long boiling with hydrochloric acid.

Chlorohydrargyrate of Xanthocobalt.—This salt is formed by adding a cold solution of chloride of mercury to a solution of the chloride of xanthocobalt. It is usually thrown down in the form of brilliant pale brownish-yellow talcose scales, which on re-solution in hot water containing a little free hydrochloric acid, separate as the solution cools in brown-yellow needles. The two forms appear to have the same chemical constitution. The salt is quite insoluble in cold, and with difficulty soluble in hot water, but the solution occurs without sensible decomposition. The chlorohydrargyrate of xanthocobalt has the formula $NO^2 . 5NH^3 . Co^2O, Cl^3 + 4HgCl + 2HO$, which requires—

	Equivs.	Calculated.	Found.
Cobalt	2	7·25	7·44
Chlorine	6	26·19	26·05

Ferrocyanide of Xanthocobalt.—This salt is precipitated almost immediately when a solution of ferrocyanide of potassium is added to one of the nitrate of xanthocobalt. We have not been able to obtain it, however, either from the chloride or the sulphate, with which the ferrocyanide of potassium gives only turbid solutions. The salt is precipitated in prismatic crystals which appear to belong to the oblique rhombic system. Its colour is a very beautiful bright orange-red, corresponding nearly with the red-orange No. 5 of the 2nd circle of Chevreul's scale. When freshly prepared, it is one of the most beautiful salts which chemistry can exhibit, but it loses some of its brilliancy of tint by keeping, and becomes a little

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duller and darker, probably from a slight decomposition upon the surface. The crystals exhibit a fine dichroism by reflexion, the ordinary image being pale reddish-orange, while the extraordinary image is bright orange. The ferrocyanide of xanthocobalt is almost insoluble in cold, and is immediately decomposed by hot or even by warm water. The crystals lose water and are partially dissolved *in vacuo*, or even *in pleno* over sulphuric acid. They can, therefore, only be dried by pressure between folds of bibulous paper. The impossibility of purifying this salt by recrystallization, and the facility with which it is decomposed, render it difficult to obtain it in a perfectly pure state.

The formula of the ferrocyanide appears to be $NO^2.5NH^3.Co^2O$, $Cy^2+FeCy+7HO$, which requires—

	Equivs.	Calculated.		Found.		
				1.	2.	3.
Cobalt ..	2	16·80	24·77	16·39	24·76	24·74
Iron	1	7·97		8·19		
Carbon..	6	10·25		10·49		
Hydrogen	22	6·26		6·14		
Nitrogen	9	35·89		35·66	35·51	

These analyses agree with the formula as well as can be reasonably expected, when the difficulty of obtaining a perfectly pure salt is taken into consideration. It is interesting to remark that in this salt, in which there is but one equivalent of basic cyanide, there are still two equivalents of cyanogen in the basic for one in the acid or electro-negative cyanide.

Sulphate of Xanthocobalt.—When pure sulphate of cobalt is dissolved in water, an excess of ammonia added, and a current of NO^x passed through the liquid, an absorption takes place, and copious fumes of carbonate of ammonia are given off. The liquid gradually assumes a dark brown-yellow colour, and frequently deposits an abundance of crystals during the passage of the current of gas. Ammonia must be added from time to time, so as to keep the solution strongly alkaline, and prevent the appearance of red vapours at the surface of the liquid. It is not necessary to apply heat, as the temperature rises from the absorption of the gas. When the operation is over, which is indicated by the colour of the liquid, the solution may be filtered and allowed to evaporate spontaneously, when a mass of brown-yellow crystals is obtained. These may be purified by re-solution in hot water with addition of a few drops of acetic acid and re-crystallization.

This method of preparing the salt is a convenient one, and large quantities may be prepared in a few hours. The time required for the completion of the oxidation depends upon the quantity of sulphate of cobalt employed, and may last from one to twelve hours. It is best to employ a rapid current of the gas. The formation of the sulphate of xanthocobalt, under these circumstances, may be represented by the equation

$$2CoO,SO^3+5NH^3+NO^3=NO^2.5NH^3.Co^2O^3,2SO^3,$$

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if we suppose the oxidizing agent to be NO^3. If, however, we consider the active agent to be NO^4, we may represent the action by the equation

$$2CoO, SO^3 + 6NH^3 + 2NO^4 + HO = NO^2 . 5NH^3 . Co^2 O^3, 2SO^3 + NH^4 O, NO^5.$$

A large quantity of free nitrite of ammonia is always formed during the process, as we believe, by the direct action of NO^3 upon ammonia and water. The addition of an acid to the mother-liquor from which the sulphate has crystallized, produces an active effervescence arising from the decomposition of the nitrite of ammonia.

The process which we have indicated has generally proved perfectly satisfactory in preparing the sulphate. It is proper to state, however, that in some experiments, made for the purpose of revision, we obtained by the process above given no sulphate of xanthocobalt, but only the nitrate. The cause of this we are at present unable to assign, and further experiments are wanting to explain so unexpected a result.

The sulphate of xanthocobalt crystallizes in thin plates, the form of which we have not been able to determine; they appear to belong to the right rhombic system. The crystals have a fine brown-yellow colour, which, however, we cannot define by means of the chromatic scale. The salt is rather soluble in hot, but much less soluble in cold water. Heat readily decomposes the neutral solution, a black powder being thrown down, while ammonia is given off. The dry salt is decomposed like the chloride.

Strong sulphuric acid dissolves the sulphate to a red oily liquid, but little deutoxide of nitrogen being given off. The addition of water to this solution causes a violent effervescence from the escape of deutoxide of nitrogen, and probably nitrous acid. There remains a red liquid consisting chiefly of the double sulphate of cobalt and ammonia, but almost always containing a little acid sulphate of purpureocobalt. Even very dilute sulphuric acid readily decomposes sulphate of xanthocobalt by boiling. Long boiling with hydrochloric acid also decomposes this salt, the products of the decomposition being, as already stated, chloride of purpureocobalt, free sulphuric acid, and deutoxide of nitrogen.

Sulphate of xanthocobalt has the formula $NO^2 . 5NH^3 . Co^2 O^3, 2SO^3 + HO$, which requires—

	Equivs.		Calculated.	Mean.	Found.	
Cobalt.....	2	59	20·55	20·68	20·69	20·68
Sulphuric acid	2	80	27·94	27·90	27·65	28·16
Hydrogen ..	16	16	5·57	5·62	5·56	5·68
Nitrogen	6	84	29·26	29·44	29·37	29·51
Oxygen	12	96	16·68	16·30		

A solution of sulphurous acid dissolves sulphate of xanthocobalt without decomposition. On boiling, however, a complete decomposition takes place, bubbles of gas are given off, and there remains a red solution of the double sulphate of cobalt and ammonia. The

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gas which is evolved produces no red vapours on contact with the air, and is probably protoxide of nitrogen. The sulphate of xanthocobalt is also decomposed by boiling with urea, an abundance of a colourless gas without odour being given off. The reactions of the sulphate are similar to those of the chloride.

Nitrate of Xanthocobalt may be prepared like the sulphate, by passing a current of NO^x into an ammoniacal solution of nitrate of cobalt. The formation of the nitrate goes on very rapidly, and crystals are usually deposited in abundance long before the oxidation is complete. It is best in this case, as in the preparation of the sulphate, to employ a pure salt of cobalt and pure ammonia, as the subsequent purification of the nitrate of xanthocobalt becomes much more easy. The equations representing the formation of the nitrate are similar to those which we have given for the sulphate.

The nitrate of xanthocobalt may also be easily prepared by the action of NO^x upon neutral, acid, or alkaline solutions of the chlorides, sulphates and nitrates of roseocobalt and purpureocobalt. We have alluded to the formation of the nitrate of xanthocobalt by this process already, and will here enter more into detail.

It is almost a matter of indifference which salt is selected, as the nitrate is prepared with nearly equal facility from all. The salt is to be dissolved in water, and to hasten the process, ammonia added; a large excess of ammonia is not necessary, but the process always goes on more rapidly in ammoniacal than in an acid or neutral solution. The current of gas resulting from the action of nitric acid upon starch or sawdust is then to be passed into the liquid, which speedily becomes hot and gradually changes its colour from violet to orange-red, and at last to orange, while orange-yellow crystals of the nitrate of xanthocobalt are precipitated. The liquid on cooling gives more crystals; the process should not be continued after the whole mass has assumed a clear orange-yellow colour. The mother-liquor from which the crystals of the nitrate of xanthocobalt have separated contains only salts of ammonia, with a little nitrate in solution. The whole process is very easy to execute, and yields a very pure nitrate. The reactions which occur in this process are remarkably beautiful, and may be expressed, in the case of the action of the gas upon the chloride and sulphate of roseocobalt, by the equations—

$$5NH^3 . Co^2 Cl^3 + 3NO^4 + 3HO = NO^2 . 5NH^3 . Co^2 O^3, 2NO^5 + 3HCl,$$

$$5NH^3 . Co^2 O^3, 3SO^3 + 3NO^4 + 3HO = NO^2 . 5NH^3 . Co^2 O^3, 2NO^5 + 3HO, SO^3.$$

It will be seen from these equations that when neutral solutions of the salts of roseocobalt or purpureocobalt are employed, hydrochloric and sulphuric acids are set free. The influence of an excess of ammonia in facilitating the process is thus easily understood. The nitrate of xanthocobalt, being much less soluble in cold water than the ammonia salts, is easily purified by re-crystallization. In treating of the sulphate and chloride of xanthocobalt, we have mentioned that the nitrate of xanthocobalt is often formed while preparing

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these salts directly. As a mode of preparation, this method is not to be recommended, but it possesses much theoretical interest. The equation which represents the action when the nitrate of xanthocobalt is formed directly by the action of NO^x upon an ammoniacal solution of the sulphate of cobalt, is possibly the following:—

$$2CoO, SO^3 + 7NH^3 + NO^3 + 3NO^4 + 2HO = NO^2 . 5NH^3 . Co^2 O^3, 2NO^5 + 2NH^4 O, SO^3 + NO^2.$$

When the chloride of cobalt is employed instead of the sulphate, other products are always formed simultaneously with the nitrate of xanthocobalt, and the reaction becomes therefore more complicated.

The nitrate of xanthocobalt crystallizes in small brilliant crystals, which according to Prof. Dana's measurement, belong to the dimetric system. The only form observed as yet is an octahedron, the angle at the base being 100° 45′ to 101° 15′.

The salt is dichrous, the ordinary image being pale orange, while the extraordinary is bright orange-yellow.

The salt has a clear brown-yellow colour, and the mass of crystals is usually very brilliant. It is quite soluble in hot, but rather insoluble in cold water; the solution is readily decomposed by boiling, with evolution of ammonia and precipitation of a heavy black powder. The dry salt is readily decomposed by heating, abundance of red vapours being given off, while a black oxide remains. The nitrate is completely decomposed by boiling with hydrochloric acid, red vapours mixed with chlorine being given off, while there remains a solution of purpureocobalt, from which crystals of this salt are deposited on cooling. When boiled with nitric acid, a similar decomposition is produced, and crystals of nitrate of roseocobalt are obtained in small quantity. It is probable that nitrate of purpureocobalt is the first product of this reaction, and that this by boiling with excess of acid, passes into the nitrate of roseocobalt. As a general rule, the quantity of nitrate of roseocobalt produced is small, and the decomposition results in the conversion of the nitrate of xanthocobalt into the nitrates of cobalt and ammonia.

Nitric acid precipitates nitrate of xanthocobalt from its solution without sensible decomposition in the cold. By long boiling acetic acid completely reduces nitrate of xanthocobalt, and a solution of cobalt is obtained which is free from ammonia-cobalt bases. Oxalic acid also reduces the nitrate by boiling, oxalate of cobalt being thrown down.

Nitrate of xanthocobalt has the formula $NO^2 . 5NH^3 . Co^2 O^3, 2NO^5 + HO$, which requires—

	Equivs.	Calculated.		Mean.	Found.		
Cobalt ..	2	59·0	18·73	18·74	18·76	18·72	18·75
Hydrogen	16	16·0	5·08	5·11	5·04	5·21	5·09
Nitrogen	8	112·0	35·55	35·50	35·73	35·50	35·27
Oxygen	16	128·0	40·64	40·55			

As the nitrate of xanthocobalt is, of all the salts of this base, that which is most easily prepared in a state of purity, and as its re-

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actions are most characteristic of the base, we shall give them in this place.

Hydrochloric acid in excess gives a buff-yellow precipitate. Alkaline carbonates give no precipitate. Ferrocyanide of potassium precipitates beautiful orange-red crystals. Ferridcyanide of potassium gives no precipitate. Cobaltidcyanide of potassium gives no precipitate. Chromate of potash gives a fine clear yellow precipitate. Bichromate of potash gives beautiful orange-red needles. Oxalate of ammonia gives a voluminous precipitate of pale yellow needles. Picrate of ammonia gives beautiful clear yellow needles. Phosphate of soda gives no precipitate. Pyrophosphate of soda gives no precipitate. Chloride of mercury gives a buff-coloured scaly precipitate. Protochloride of tin gives, after a short time, granular yellow crystals. Bichloride of platinum gives an orange-yellow precipitate. Terchloride of gold gives, after addition of hydrochloric acid and standing, yellow needles. Iodide and bromide of potassium give no precipitates.

Oxalate of Xanthocobalt is precipitated when a solution of oxalate of ammonia is added to one of the chloride, nitrate, or sulphate of the base. After a very short time yellow acicular crystals make their appearance, the separation being greatly facilitated by strongly agitating the solution. The precipitate is to be thrown on a filter, well washed with cold water and dried, first by pressure and afterwards *in pleno* over sulphuric acid. As thus prepared, the salt has a pale yellow colour, and consists of fine needles, the form of which cannot be determined, even under the microscope. It is nearly insoluble in cold and but very slightly soluble in hot water. The solution is readily decomposed by boiling. The insolubility of this oxalate and its characteristic appearance render it of great value in detecting the presence of salts of xanthocobalt.

Oxalate of xanthocobalt has the formula $NO^2.5NH^3.Co^2O^3$, $2C^2O^3+5HO$, which requires—

	Equivs.	Theory.	Found.	
Cobalt.....	2	21·14	21·01	21·06
Oxalic acid..	2	25·81	25·70	25·99

[To be continued.]

On the Preparation of Iodide of Potassium. *By* J. Liebig.

Iodide of potassium is very commonly prepared by treating 3 parts by weight of iodine with metallic iron and water, mixing the solution of protiodide of iron with 1 part of iodine, and after this is dissolved, adding caustic potash or carbonate of potash. On the large scale this process has some inconveniences, which may be got rid of in the following manner:—

The solution of protiodide of iron is first of all prepared as above, but then the third part of the iodine contained in it is dissolved, not in this iron solution, but in dilute solution of potash (or in solution of soda when iodide of sodium is to be prepared); the precipitation

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with the protiodide of iron is then commenced. The quantity of the caustic lye must be somewhat less than is necessary for precipitation, and this is completed at last by careful addition of alkaline carbonate. Heat or boiling is unnecessary for the precipitation. The pasty, inflated precipitate is, or appears, very heterogeneous in its mass; but when it is left to stand for a night, with occasional stirring, the protoxide unites with the oxide completely to form *Æthiops martialis*, which may be freed from all iodide of potassium by two or three lixiviations. When instead of 3, only 2 parts of iodine are employed, and then 1 part is dissolved in caustic lye, with which the first solution is precipitated, a very pure hydrated oxide of iron is obtained, which may be washed just as well as the *Æthiops*.—Liebig's *Annalen*, c. p. 339.

On the Action of Perchloride of Phosphorus upon some Inorganic Acids. *By* Hugo Schiff.

Persoz and Bloch have described several products formed by the action of perchloride of phosphorus upon inorganic acids. If dry sulphurous acid gas be passed over perchloride of phosphorus, a fluid is obtained, which, according to Persoz, Bloch, and Kremers, is sulphite of perchloride of phosphorus, $PCl^5\,S^2\,O^4$.

The author found that this fluid is decomposed by fractional distillation; the more volatile portion passing at 147°·6 F. contained only traces of phosphoric acid; the rest, which boiled at 230° F., was perchloride of phosphoryle, $PO^2\,Cl^3$.

The more volatile distillate has an extraordinary refractive power like sulphuret of carbon; it is decomposed by water, and still more readily by alkalies into muriatic and sulphurous acids; with alcohol it gives muriatic and æthylosulphurous acids. It has a suffocating odour like sulphurous acid. This substance is

Perchloride of Thionyle, $\left.\begin{matrix}S^2\,O^2\\Cl^2\end{matrix}\right\}$.—The author calls the group $S^2\,O^2$ thionyle, and regards sulphurous acid in its salts as $\left.\begin{matrix}S^2\,O^2\\H^2\end{matrix}\right\}O^4$. Anhydrous sulphurous acid is then $S^2\,O^2$, O^2.

Thionylamide, $N^2\,(S^2\,O^2)\,H^4$, is produced when the preceding perchloride is brought in contact with dry ammonia, $\left.\begin{matrix}S^2\,O^2\\Cl^2\end{matrix}\right\}+4NH^3 = N^2\begin{matrix}S^2\,O^2\\H^2\\H^2\end{matrix}+2NH^4\,Cl$. The reaction is so violent that the product acquires a reddish-brown colour with separation of sulphur. This is avoided by refrigeration and moderation during the passage of the gaseous ammonia, and then a white, non-crystalline body is obtained, which parts with muriate of ammonia to water, and becomes completely decomposed therewith. The author has not obtained the amide pure, but he has no doubt that the body obtained is a mixture of thionylamide and muriate of ammonia.

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Aniline behaves in a similar manner towards perchloride of thionyle.

According to the author, the so-called anhydrous bisulphite of ammonia (H. Rose's sulphitammon) contains thionylaminic acid, $NH^2 \left.\begin{matrix} S^2 O^2 \\ H \end{matrix}\right\} O^2$.

The action of anhydrous sulphuric acid upon pentachloride of phosphorus is exactly similar to that of sulphurous acid. The bisulphate of perchloride of phosphorus described by Persoz and Bloch, $PCl^5 S^2 O^6$, is accordingly nothing but a mixture of $PO^2 Cl^3$ and $S^2 O^4 Cl^2$, the so-called chlorosulphuric acid. If we admit the existence in sulphuric acid of a bibasic radical ($S^2 O^4$, sulphuryle of Laurent and Gerhardt), we have,—

$S^2 O^4, O^2$ anhydrous sulphuric acid,	representing	$H^2 O^2$
$\left.\begin{matrix} S^2 O^4 \\ H^2 \end{matrix}\right\} O^4$ hydrated sulphuric acid	,,	$\left.\begin{matrix} H^2 \\ H^2 \end{matrix}\right\} O^4$
$\left.\begin{matrix} S^2 O^4 \\ Cl^2 \end{matrix}\right\}$ perchloride of sulphuryle (chlorosulphuric acid)	,,	$\left.\begin{matrix} H^2 \\ H^2 \end{matrix}\right\}$
$\left.\begin{matrix} S^2 O^4 \\ Br^2 \end{matrix}\right\}$ perbromide of sulphuryle (bromosulphuric acid)		
$N^2 \left\{\begin{matrix} S^2 O^4 \\ H^2 \\ H^2 \end{matrix}\right.$ sulphamide (Regnault)	,,	$N^2 \left\{\begin{matrix} H^2 \\ H^2 \\ H^2 \end{matrix}\right.$
$NH^2, \left.\begin{matrix} S^2 O^4 \\ H \end{matrix}\right\} O^2$ sulphaminic acid (sulphat-ammon, H. Rose)	,,	$\left.\begin{matrix} NH^4 \\ H \end{matrix}\right\} O^2$

The tungstate of perchloride of phosphorus of Persoz and Bloch also is no determinate, simple compound. From the reddish-brown fluid obtained by treating tungstic acid with perchloride of phosphorus, perchloride of phosphoryle, $PO^2 Cl^3$, may be easily distilled. The residue appears to be binoxychloride of tungsten, $W^2 O^4 Cl^2$.

The product obtained by treating molybdic acid with perchloride of phosphorus behaves in exactly the same way.

If antimonic acid be heated with perchloride of phosphorus, only the so-called basic water of that acid reacts; muriatic acid is evolved in fumes, and $PO^2 Cl^3$ is distilled off; the residue is anhydrous antimonic acid.

When perchloride of phosphorus is heated with anhydrous phosphoric acid, perchloride of phosphoryle is obtained,—thus $3PCl^5 + P^2 O^{10} = 5PO^2 Cl^3$.

When perchloride of phosphorus is distilled with oxychloride of chromium, a small quantity of perchloride of chromium is formed, whilst the greater part of the oxychloride distils off unchanged. A formation of perchloride of chromium, probably in accordance with the equation

$$Cr^2 O^4 Cl^2 + 2PCl^5 = 2PO^2 Cl^3 + 3Cl + 3\,crCl \left(cr = \frac{2Cr}{3}\right),$$

also takes place when the two substances are heated in the water-bath in closed tubes. In this case, however, a simultaneous reaction

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of the perchloride of phosphoryle formed, upon the rest of the oxychloride of chromium, occurs, for on opening the tubes, when a great quantity of chlorine gas escapes, there is found, together with the perchloride of chromium, another body, which in its external appearance and in its properties exactly resembles the mixture which Casselmann obtained by the mutual action of those two substances. On heating it, oxychloride of chromium distils off, and finally, when strongly heated, it becomes converted into perchloride of chromium. Perchloride of phosphorus has no action upon carbonic acid and sulphuret of carbon.—Liebig's *Annalen*, cii. p. 111.

On Iodide of Aluminium. *By* R. Weber.

Wöhler has shown that iodide of aluminium cannot be prepared by the same method by which Oerstedt in 1820 obtained the chloride, and Löwig subsequently the bromide of aluminium, namely, by mixing alumina with charcoal and igniting the mixture in a current of chlorine or bromine.

By treating metallic aluminium with iodine, the author has obtained iodide of aluminium, $Al^2 I^3$. Some filings of aluminium were placed in a glass tube about 7 centimetres in length closed at one end; dry iodine was then put in and the tube sealed with the lamp. It is advisable to employ 1 part of aluminium to 10–11 parts of iodine. At the ordinary temperature the combination perhaps only takes place slowly; the iodine in contact with the aluminium soon adheres slightly to the walls of the tube, and separates therefrom when struck, leaving behind a brown spot.

If the tube be now carefully heated, the combination is effected with a strong evolution of light and heat; the granules of aluminium burn in the tube with a beautiful violet light; the iodide of aluminium formed constitutes on cooling a solid mass, with a strong brown colour from the presence of iodine. If a slight excess of aluminium were employed, all that is necessary is to heat the tube again gently, especially at the point where the metal was placed, and to drive the iodine there by the flame so as to free the compound from excess of iodine; the compound then appears mixed with aluminium as a dingy white crystalline mass.

The iodide of aluminium thus prepared may easily be collected at the end of the tube; the tube is then bent by the lamp, (or a bent tube may be employed from the commencement), and the iodide of aluminium is heated, when it fuses, soon boils, and sublimes in delicate snow-white laminæ into the cold part of the tube.

The iodide of aluminium thus separated from free iodine and the excess of aluminium forms dazzling white crystalline laminæ, which fuse into an extremely liquid fluid, boiling readily when further heated. On cooling it forms a solid, white, radiately crystalline mass. In the air the compound fumes strongly and deliquesces into oily drops by attracting water; it soon colours paper purple-red, and dissolves in water with a strong evolution of heat. When heated in the air, it is decomposed very readily; iodine separates

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under these circumstances, so that it is scarcely possible to transfer it when fused from one tube to another without alteration, as the mass is always coloured brown by some separated iodine. If a few granules of aluminium be put into the second tube and first heated, the whole amount of free iodine is absorbed, and the compound may then be again obtained perfectly white. Analysis gave—

				Average.		
Iodide of silver	2·611	2·545	2·947, or I	93·20	3	93·10
Alumina	0·203	0·199	0·231, or Al	7·12	2	6·90

Iodide of aluminium behaves exactly like the chloride. It dissolves in water with strong evolution of heat, forming a fluid which rapidly becomes brown in the air. It is also soluble in absolute alcohol.

The aqueous solution may be evaporated *in vacuo* over sulphuric acid, and under certain circumstances a perfectly white mass may thus be obtained. The iodide of aluminium is treated with little water so as to produce a clear oily solution; this is then quickly placed under the bell of the air-pump, and as complete a vacuum as possible is produced. A radiately crystalline film is soon formed, and in a short time this becomes an enamel-like mass. When touched with a glass rod, the mass, which is still tenaciously fluid, then often solidifies with a distinct evolution of heat. The solid mass remains without alteration under the bell-glass with sulphuric acid; it does not fume in the air, deliquesces readily, and dissolves without residue in water. When heated in a glass tube it is decomposed; water, hydriodic acid, and free iodine are evolved, leaving alumina in the residue. It is therefore probably a hydrate of the periodide; the author proposes to determine its composition more exactly.

Iodide of Potassium and Aluminium, $KI + Al^2I^3$, is produced when iodide of aluminium in the form of vapour is brought into contact with heated iodide of potassium in a sealed tube. This compound has the appearance of a waxy, transparent, crystalline mass, which fuses readily, but appears to be very difficult to volatilize. It is not decomposed by being strongly heated, but only parts with a small excess of iodide of aluminium with great difficulty; for this purpose the temperature must be raised until the softening of the glass. In water it dissolves without residue, producing much heat. Analysis:—

I	88·59	4	88·42
Al	5·26	2	4·77
K	5·76	1	6·81

Poggendorff's *Annalen*, ci. p. 465.

Note on a New Anilide of Salicylous Acid. *By* L. Chichkoff.

On heating equal volumes of salicylous acid and aniline under the ordinary pressure, an elimination of water is soon observed, and the liquid mixture solidifies on cooling. The body thus obtained is insoluble in water, but very soluble in alcohol, and cry-

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stallizes in fine bright yellow crystals. It is fusible at a temperature below 212° F.

By heating this body with acids or alkalies, the primitive bodies are regenerated, which proves that the new compound may be represented by

$$C^{14} H^6 O^4 + C^{12} H^7 N - H^2 O^2.$$

Its analysis gave—

	I.	II.		Calculated.
C	78·70	78·60	26	79·10
H	6·00	6·00	11	5·50
N	7·06	..	1	7·10
O	..	..	2	8·30

This body is isomeric with benzanilide, from which it differs completely in its properties. An alcoholic solution of salicylous anilide is not decomposed by sulphuretted hydrogen.—*Comptes Rendus*, August 24, 1857, p. 272.

ANALYTICAL CHEMISTRY.

On the Detection of Strychnine. *By* Richard Hagen.

The author has investigated this subject in the laboratory and under the guidance of von Gorup-Besanez. He was induced to this by the statements of von Sicherer, that the well-known reaction with bichromate of potash and concentrated sulphuric acid fails when the strychnine is mixed with tartrate of antimony or tartrates in general, or with free tartaric acid.

He first ascertained that the reactions with bichromate of potash, or ferridcyanide of potassium and concentrated sulphuric acid, and with peroxide of lead and sulphuric acid containing nitric acid, never fail when pure strychnine is employed, whether by itself or mixed with a large quantity of sugar, if proper care be taken; this is particularly important, as these reactions have been described as uncertain by incompetent persons in various medical journals. He then passed to the testing of some salts of strychnine.

I. With nitrate of strychnine the reaction with bichromate of potash or peroxide of lead and concentrated sulphuric acid, occurs just as distinctly and persistently as with pure strychnine.

II. This is also the case with muriate of strychnine, with which the characteristic colour even appears to be more beautiful than with pure strychnine or the nitrate.

III. Acetate of strychnine also gives the above mentioned reactions with equal distinctness.

Mixtures of pure strychnine and tartrate of antimony in various proportions were tested with bichromate of potash and sulphuric acid.

a. Of a mixture of equal weights of strychnine and tartrate of antimony, weighing 2 grs. in all, a fourth part was put into a watch-glass, and treated with 4 or 5 drops of concentrated sulphuric acid; the whole was then worked into a uniform mass by means of a small pestle. On the addition of a drop of a moderately concentrated

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solution of bichromate of potash to this mass, a very beautiful bluish-violet stripe was immediately formed around it. On moving the watch-glass to and fro, the coloration spread through the whole mass, and increased in intensity on the addition of another drop of the solution of bichromate of potash; the reaction persisted as long as with pure strychnine, the blue colour gradually passing to violet and then to red.

b. With a mixture of 1 part by weight of strychnine with 10 parts of tartrate of antimony, the reaction occurred just as rapidly and certainly, and persisted nearly as long as with the preceding mixture.

c. With 1 part of strychnine and 20 parts of tartrate of antimony, the reaction lost somewhat in duration, but not in certainty and beauty.

d. With 1 part of strychnine and 30 parts of tartrate of antimony, the duration of the reaction was plainly diminished; it nevertheless occurred quite distinctly. Towards the end of the reaction the mass acquired a greenish tinge.

With a mixture of 1 part of strychnine with 60 parts of tartrate of antimony, the reaction was still distinctly recognizable by a practised eye, but disappeared very rapidly, the fluid acquiring a greenish colour. The same result was obtained with mixtures of tartaric acid and strychnine.

From these experiments it appears that this reaction for strychnine is one of the most sensitive with which we are acquainted, and that von Sicherer's statements must be founded in error. As however it could not be supposed that they had no foundation in fact, the author tried mixtures of salts of strychnine with tartrate of antimony in various proportions. He obtained the following results:—

With an intimate mixture of 1 part of nitrate of strychnine and 20 parts of tartrate of antimony, the reaction with bichromate of potash and sulphuric acid does not occur; the mass almost instantly acquires a green colour. But up to these proportions the reaction occurs even here.

With muriate of strychnine, the reaction is still recognizable with mixtures of 1 part of the salt with 30 parts of tartrate of antimony. This is the case also with acetate of strychnine.

The reaction for strychnine with peroxide of lead and sulphuric acid is not in the least affected by the presence of tartrate of antimony, other tartrates, or free tartaric acid, whether pure strychnine or its salts be employed in the experiments. The reaction occurs with perfect certainty with proportions of 1 to 60; the author considers pure sulphuric acid to be preferable to that containing nitric acid, when tartrates are present.

From these experiments it appears that the presence of tartrates, tartrate of antimony, or free tartaric acid with pure strychnine, does not affect the reaction with bichromate of potash and sulphuric acid; but that it becomes less sensitive with nitrate of strychnine, and fails altogether with an exess of tartrate of antimony. The probable reason of this is, that the nitric acid set free by the action of the sulphuric acid decomposes the tartaric acid, giving rise to

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products of decomposition which exert a violent reducing action upon the chromic acid.

On the other hand, the characteristic reaction is produced with perfect certainty by peroxide of lead and sulphuric acid, even in the presence of tartrates, although nitrate of strychnine be employed.

As a matter of course, when in judicial cases nitrate of strychnine and tartaric acid coexist in the substance to be investigated, by the employment of the process of Stass, the strychnine is obtained as such, and not in the form of a salt, so that the above facts would have no influence upon the result. In examining a powder consisting of nitrate of strychnine and tartrates, the nitrate must be converted into pure strychnine, or the reaction with peroxide of lead and sulphuric acid must be employed; this, indeed, should be preferred in all cases when there are no data regarding the nature of the substance under investigation.—Liebig's *Annalen*, August 1857, p. 159.

On the Behaviour of various Substances towards pure fused Chlorate of Potash. *By* Professor Böttger.

Pure fused chlorate of potash is an excellent reagent for manganese, being especially fitted for the detection of manganese in organic bodies. The presence of the smallest, scarcely ponderable trace of manganese may be instantly recognized, even when a small fragment (the size of a pea) of an organic body, which is to be tested for manganese, is thrown upon the surface of a small quantity of fluid chlorate of potash in a test-glass, by the fact that after the combustion of the body, the perfectly cold saline mass has a more or less rose-red or peach-blossom colour in consequence of the formation of hypermanganate of potash. To make sure that the chlorate of potash employed as a reagent is perfectly free from manganese (the ordinary commercial salt almost always containing that metal), a small quantity (1 drm.) of it is fused in a test-glass, and a few particles of pure carbon (prepared from perfectly colourless sugar-candy) are thrown into it. If the salt remain perfectly colourless on cooling, it is adapted for the purpose here referred to; but should it appear of a slight rose colour, it contains traces of manganese, and must be rejected.

When pure chlorate of potash is heated by an ordinary spirit-lamp in a rather wide test-tube until it becomes perfectly fluid and begins to evolve oxygen gas, and small quantities of the following substances are thrown into it, the following results are obtained:—

Beech- and boxwood charcoal, and small fragments of cork charcoal, burn away with an intense light, jumping up and down, and leave a saline mass of a reddish colour; whilst some kinds of pine- and fir-woods, treated in the same way, leave the saline mass completely colourless when cold.

Some specimens of graphite, treated as above, were found to contain manganese.

Bitartrate of potash and tartaric acid burn with a violet light; the samples tested proved to be free from manganese.

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Oxalic acid, as was to be expected, did not ignite.

Peroxide of iron is not converted into ferrate of potash; it remains perfectly unaltered, and only causes a violent evolution of oxygen gas; protoxide of iron ignites and burns to peroxide.

Fragments of the size of a pea of ordinary roll-sulphur, burn with an extremely intense white light to form sulphate of potash; peroxide of phosphorus in the same way forms phosphate of potash.

Phosphorus must only be employed in small fragments of the size of a pin's head, in a perfectly dry state, and always with care; the combustion takes place with evolution of an extremely intense white light.

Pulverulent antimony burns with scattering sparks.

Iron-filings burn away with a fine light when the chlorate of potash has been so far heated that the evolution of oxygen gas begins to be violent; glowing globules of sesquioxide of iron are formed, and usually pierce through the bottom of the test-tube, for which reason great caution is to be recommended.

Metallic arsenic burns, diffusing an intense white light, and forming arseniate of potash.

Powder of bismuth does not ignite, but is gradually converted into oxide of bismuth.

White sugar-candy burns with an extremely beautiful violet light, which finally becomes white.

Lead-filings have no action; carbonate of lead becomes converted into peroxide of lead.

Platinum-black and fine spongy platinum burn with a very slight scattering of sparks.

Fragments of tin-foil are burnt with difficulty, and with a scarcely perceptible scattering of sparks, and only when the evolution of oxygen begins to grow violent; it forms peroxide. Tin-dust behaves in the same way, as does silver-dust (true silver-bronze).

Very fine copper-dust (true copper-bronze) burns briskly to form oxide; this is also the case with false gold-bronze (an alloy of copper and zinc).

Paris blue burns with a strong, beautiful, violet light, leaving peroxide of iron.

Crystallized gallic acid detonates violently, with a strong evolution of light; hence great caution is necessary.

Indigo burns with an extremely intense white light.

Some samples of commercial iodine left a slightly reddish saline mass; they consequently contained manganese.

Black sulphuret of antimony in powder burns quietly with a yellowish white light.

Dry extract of logwood burns with a very intense light, as does also gamboge, with evolution of a black smoke.

Caoutchouc burns with an exceedingly intense light, as soon as the evolution of oxygen begins to be tolerably strong; great heat is evolved, so that the bottom of the test-tube is not unfrequently melted.

Tea-leaves impart to the mass a tolerably strong red colour, they therefore contain manganese.—Buchner's *Neues Repert.* vi. p. 247.

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THE CHEMICAL GAZETTE.

No. CCCLXI.—November 2, 1857.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On a Compound of Silver Analogous to Purple of Cassius. By H. Schulz.

By bringing in contact hydrated protoxide of tin or protosalts of tin and a solution of nitrate of silver, a compound of silver analogous to the purple of Cassius is obtained. For the preparation of this the author proceeded as follows:—

Tinfoil was put into a vessel half-filled with very dilute nitric acid and surrounded with cold water, and frequently agitated for 24 hours; the fluid was then filtered from the undissolved tin, hydrated protoxide of tin was thrown down from the filtrate by the addition of carbonate of soda, collected on a filter, and sufficiently washed. The hydrated protoxide of tin was also partly obtained by precipitation from a solution of protochloride of tin by carbonate of soda, and this method was found to be more advantageous than that given above. When nitric acid was employed for the preparation of the hydrated protoxide of tin, sesquioxide is also formed, although only in small quantity; this, from its extraordinarily slimy nature, stuffed up the pores of the filtering paper, and thus not only rendered its washing difficult, but sometimes even impossible.

The author also prepared a neutral solution of oxide of silver in nitric acid. This solution he then added to the hydrated protoxide of tin suspended in water by constant stirring so as to form a milky fluid, as long as any reaction was perceptible, so that solution of silver was present in excess in the mixture. On the contact of the two reagents, the hydrated protoxide of tin became instantly converted into a dark brown body, which settles and may be collected when the fluid is slightly heated. When this body had been sufficiently washed, the author first investigated the filtrate from it, which contained silver in excess but no tin.

The brownish-black precipitate during desiccation acquired a colour, both on the surface and in the fracture, possessing a metallic lustre and a striking resemblance to bronze. In the form of powder it was nearly black. After being dried, even when this is done without the aid of external heat, this compound forms a solid, compact mass, which is hard and brittle, and possesses a conchoidal

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fracture. When the compound is calcined metallic silver separates. The analysis of this body gave—

Loss when heated to 320° F.....	3·1 per cent.	water.
„ by calcination	4·57 „	oxygen.
„ during reduction in hydrogen gas,		
a. of substance dried at 212° F.	16·59 „	
b. of calcined substance.....	12·00 „	
Oxide of tin 55·51=.....	43·4 „	tin.
Chloride of silver 52·53=.....	39·6 „	silver.

It may be assumed that the loss of 3·1 per cent. experienced during heating from 212° to 320° F. is to be regarded as water, and the loss of 4·57 per cent. during the calcination of the substance dried at 212° F. as water plus oxygen from the silver. The former number deducted from the latter, would consequently give the amount of oxygen of the silver, namely 1·47 per cent. The further loss of weight of 16·59 per cent. experienced during the reduction of the substance dried at 212° F. must then be regarded as due to the elimination of the water and of the oxygen of the silver and oxide of tin, whilst the loss of 12 per cent. in the current of hydrogen might be regarded as due only to the evolution of the oxygen belonging to the oxide of tin alone. According to this the results of the analysis would stand as follows:—

Water..... =	3·1	per cent.	
Oxygen from silver	1·47	„	} total oxygen 13·47 per cent.
Oxygen from tin..	12·00	„	
Silver.....	39·6	„	
Tin.....	43·4	„	
	99·57	per cent.	

Or

3·1	per cent.	water.
41·7	„	silver + oxygen.
55·4	„	tin + oxygen.

These numbers correspond with the formula

$$Ag^2O, SnO, 3SnO^2 + 3HO.$$

Behaviour of this Compound towards Nitric Acid.—Dilute nitric acid was poured over the substance and left in contact with it for 24 hours in the cold; the undissolved portion was then separated by filtration; no tin was dissolved. When digested with nitric acid with the assistance of heat, all the tin also remained as oxide, whilst nitrate of silver was dissolved. The process will be rendered intelligible by the following equation:—

$$Ag^2O + SnO + 3SnO^2 + 3HO$$

and $$3NO^5HO = 2(AgO\,NO^5) + 4SnO^2 + NO^3 + 6HO.$$

Behaviour with Muriatic Acid.—When muriatic acid is poured over it, the colour instantly becomes paler. If it be heated to boiling, laminæ of metallic silver are deposited, covering the walls of the vessel with a specular coat. The fluid separated from the undissolved portion was divided into two parts, one of which was

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mixed with an excess of ammonia, the other neutralized by ammonia and mixed with sulphuret of ammonium. The ammonia precipitated a white body, which only dissolved partially in an excess of the precipitant; the sulphuret of ammonium produced a precipitate of an impure yellow colour, which immediately disappeared again for the most part on the addition of a large quantity of sulphuret of ammonium, leaving a brownish-black precipitate.

On adding sulphuret of ammonium to the ammoniacal solution, and subsequently supersaturating it with muriatic acid, it furnished a yellow precipitate, whilst the portion not taken up by ammonia, when dissolved in muriatic acid and neutralized by ammonia, gave a brownish-black precipitate with sulphuret of ammonium.

These experiments prove the simultaneous presence of proto- and perchloride of tin in the solution in muriatic acid, and consequently the pre-existence of protoxide and peroxide of tin in the compound in question, whilst the separation of the silver demonstrates its presence as protoxide with certainty.

The body originally formed in the cold after the addition of muriatic acid was therefore very probably the same as that which is produced when protoxide of silver is treated by itself with muriatic acid, and which may undoubtedly be regarded as protochloride of silver, although the existence of this has not yet been confirmed by analysis. The deposition of metallic silver which afterwards takes place on the application of heat, indicates a decomposition of the protochloride of silver into perchloride and metallic silver,—

$$Ag^2Cl = AgCl + Ag.$$

The behaviour of the body towards muriatic acid may therefore be expressed by the following equation:—

$$Ag^2O + SnO + 3SnO^2 + 3HO \text{ and } 8ClH = Ag^2Cl + SnCl + 3SnCl^2 + 11HO.$$

Behaviour with Sulphuric Acid.—When boiled with dilute sulphuric acid, the compound is decomposed into stannic acid, protosulphate of tin, sulphate of silver, and metallic silver. When the heat is continued, the metallic silver dissolves with evolution of sulphurous acid, whilst peroxide of tin remains. When concentrated sulphuric acid is employed, the whole compound is easily dissolved by boiling. The decomposition is therefore expressed as follows:—

$$Ag^2O + SnO + 3SnO^2 + 3HO \text{ and } 7SO^3HO = 2AgO, SO^3 + SnO, SO^3 + 3SnO^2SO^3 + SO^2 + 10HO.$$

Ammonia extracts only oxide of silver from the compound, but no tin; the residue contains silver, but it remains unsettled whether it is only partially oxidized, namely as silver plus protoxide of silver, or completely oxidized, as protoxide of silver; it also contains protoxide and peroxide of tin.

Solution of Potash extracts oxide of tin, but no silver.

From the behaviour of the compound, as above described, with ammonia, solution of potash, nitric acid, sulphuric acid, and muriatic

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acid, it follows therefore with perfect certainty, that it contains protoxide of silver, stannic acid, and protoxide of tin. The author therefore assumes the following formula as the expression of the composition of this compound:—

$$(Ag^2O, SnO, 3SnO^2 + 3HO).$$

From the Author's *Inaugural Dissertation*, Göttingen, 1857.

Researches on the Ammonia-cobalt Bases.

By WOLCOTT GIBBS *and* F. A. GENTH.

[Concluded from page 392.]

Theoretical Considerations.

The empirical constitution of the ammonia-cobalt bases being, as we believe, established, it remains to offer an exposition of our views of their theoretical structure. Claudet* and Weltzien† have endeavoured to reduce the salts of roseocobalt and luteocobalt to the type of ammonium, while Fremy has abstained from adopting any particular theory, and gives, without comment, the results of his analyses in the shape of empirical formulæ. Claudet's view is necessarily erroneous, from the fact that his formula for what we term the chloride of purpureocobalt is incorrect, inasmuch as he assigns to it 16 in place of 15 equivalents of hydrogen. Our own numerous analyses, as well as those of Rogojski and Gregory, have clearly shown that the number of equivalents of hydrogen is fifteen.

For an exposition of Weltzien's views we must refer to his paper; they appear to us wanting in simplicity, since they require us to admit, not merely an equivalent replacement of hydrogen by ammonium and cobalt, but even that the compound ammonium thus formed may replace cobalt in its sesqui-combinations. Thus, according to Weltzien, the formula of nitrate of luteocobalt is—

$$\left.\begin{matrix} N\{ & H \\ & NH^4 \\ & NH^4 \\ & Co \end{matrix}\right\} O^3 + 3NO^5,$$
$$\left.\begin{matrix} N\{ & H \\ & NH^4 \\ & NH^4 \\ & Co \end{matrix}\right\}$$

which is obviously reducible to the type $R^2O^3 + 3NO^5$.

By adopting Gerhardt's view of the constitution of the sesquioxides, Rogojski reduces the formula of chloride of luteocobalt, $6NH^3 . Co^2Cl^3$, for the form $2NH^3 . coCl$, in which co represents cobalt with $\frac{2}{3}$ of its usually received equivalent. To this body he gives the name dicobaltinamin, and considers it analogous to the chlorides of diplatosamin and palladiamin, $2NH^3 . PtCl$ and $2NH^3 . PdCl$.

* Phil. Mag. (4) ii. 253.

† Annalen der Chemie und Pharmacie, xcvii. 19.

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This view applies very well to several other salts of luteocobalt, as for example, the bromide, iodide, nitrate, and chloroplatinate, the formulæ of which become—

$2NH^3 . coBr$	or N^2H^5co, HBr
$2NH^3 . coI$	N^2H^5co, HI
$2NH^3 . coO, NO^5$	N^2H^5co, HO, NO^5
$2NH^3 . coCl + PtCl^5 + 2HO$	$N^2H^5co, HCl + PtCl^2 + 2HO$

We have remarked already that the compound $6NH^3 . Co^2 Cl^3 + 6NH^3 . CO^2 O^3, 3SO^3$, which Rogojski describes, and to which he attributes the formula

$$2NH^3 . coCl + 2NH^3 . coO, SO^3, \text{ or } N^2H^5co, HCl + SO^4H^2, 2N^2H^5co,$$

has no real existence, but is merely a mixture of the chloride and sulphate which are isomorphous salts. Rogojski's parallel between this and the sulphate of Gros's base, which according to Gerhardt's view has the formula

$$N^2 H^4 pt^2, 2HCl + N^2H^4 pt^2, SO^4 H^2,$$

is consequently illusory.

On the other hand, moreover, it must be remembered that Rogojski's view applies only to the compounds of luteocobalt, and fails entirely to reduce the formulæ of the other cobalt bases to more simple expressions, since it requires us, in these cases, to admit fractions of equivalents. Thus the formula of the chloride of purpureocobalt becomes on this view

$$N^{\frac{5}{3}}H^5 co\, Cl,$$

while that of its chloroplatinate must be written

$$3N^{\frac{5}{3}}H^5 co\, Cl + 2PtCl^2.$$

Even in the case of those compounds of luteocobalt which contain water, Rogojski's view ceases to give simple expressions, since in the majority of these the number of equivalents of water is not divisible by three. The difficulty becomes still greater in the case of the compounds of xanthocobalt. We have therefore no hesitation in rejecting Rogojski's theory as too limited in its application.

We consider the ammonia-cobalt bases as conjugate compounds of sesquioxide, sesquichloride, &c. of cobalt, the five or six equivalents of ammonia, or of ammonia and deutoxide of nitrogen, forming the conjunct, and serving to give to the sesquicompound of cobalt the degree of stability which it possesses in this class of bodies. Accordingly we should prefer to write the formula of chloride of luteocobalt

$$6NH^3 \frown Co^2 . Cl^3,$$

employing the connecting circumflex, as Kolbe has suggested, as a symbol of conjugation. Adopting this view, we have the following conjugate radicals, which we assume as existing in the ammonia-

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cobalt bases precisely in the same sense in which we assume Co^2 as existing in the sesquichloride and sesquioxide of cobalt:—

Roseocobalt	$5NH^3.Co^2$
Purpureocobalt	$5NH^3.Co^2$
Luteocobalt	$6NH^3.Co^2$
Xanthocobalt	$NO^2.5NH^3.Co^2$.

We may, however, remark that while this view offers a satisfactory explanation of the fact that two of the ammonia-cobalt bases are triacid, forming in all cases neutral compounds with three equivalents of acid, two are biacid bases, and of these latter, one, namely purpureocobalt, forms acid compounds with four equivalents of acid.

In these cases we meet with the same difficulty which occurs with the ordinary salts of sesquioxides; thus sesquioxide of iron may unite with one, two, or three equivalents of acid, though there appear to be three in the neutral salts. While some chemists assume that salts of sesquioxide of iron containing one or two equivalents of acid are basic, others consider the different equivalents of oxygen as united in different modes, so that the oxide may be, according to circumstances,

$$Fe^2O^3$$
$$Fe^2O^2.O$$
$$Fe^2O.O^2.$$

Peligot's theory of the constitution of sesquioxide of uranium is another case in point; as this oxide unites with but a single equivalent of acid, it may be considered, as Peligot has shown, as the oxide of a radical, $U^2O^2.O$, so that in this case also, the rule that a base unites with as many equivalents of acids as the base itself contains equivalents of oxygen, is satisfied.

To explain the biacid character of two of the ammonia-cobalt bases, we may therefore assume in them the existence of secondary radicals containing oxygen. Thus in purpureocobalt and xanthocobalt the primary radicals are

$$5NH^3.Co^2$$
$$NO^2.5NH^3.Co^2;$$

while the secondary radicals are

$$5NH^3.Co^2O$$
$$NO^2.5NH^3.Co^2O.$$

The oxides on this view are

$$5NH^3.Co^2O.O^2$$
$$NO^2.5NH^3.Co^2O.O^2,$$

and are consequently of the form RO^2, so that their biacid character is explained. The doctrine of polyacid bases is by no means new;

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it is in fact contained in the empirical law above referred to, that there are in neutral salts as many equivalents of acid as there are of oxygen in the base, bearing in mind, however, that the oxygen in the base must be outside of the radical. The ammonia-cobalt bases, like the conjugate metals produced by the union of ethyle, methyle, &c., with antimony, arsenic, and bismuth, serve, however, to place the doctrine of polyacid bases upon the same footing as that of the polybasic acids, so that the two theories are in this way complementary to each other. From this point of view it is interesting to remark, that the chloroplatinates and double cyanides of the ammonia-cobalt bases follow the same law as the oxygen salts; thus we have

$$6NH^3 . Co^2 Cl^3 + 3PtCl^2$$
$$5NH^3 . Co^2 Cl . Cl^2 + 2PtCl^2$$
$$NO^2 . 5NH^3 . Co^2 O . Cl^2 + 2PtCl^2$$
$$6NH^3 . Co^2 Cy^3 + Co^2 Cy^3$$
$$NO^2 . 5NH^3 . Co^2 O . Cy^2 + FeCy.$$

In point of fact, the presence of but two equivalents of bichloride of platinum in the chloroplatinate of purpureocobalt first led us to suspect that the true oxygen salts of this base would be found to contain but two equivalents of acid.

Two other points require special notice in this connexion. We have already shown that the oxide of purpureocobalt, in at least two cases, is capable of uniting with *four* equivalents of acid so as to form feebly acid salts. We consider these salts the true bi-salts of the base, and not as double salts of purpureocobalt and water. In other words, we hold that they bear the same relation to the neutral salts of the base which bichromate of potash does to the neutral chromate. If this view be correct, we may perhaps expect to find salts of roseocobalt or luteocobalt containing *six* equivalents of acid. The only acid salt of luteocobalt hitherto discovered is the carbonate, but this in reality, in our view, is a double salt of luteocobalt and water, and has the formula

$$6NH^3 . Co^2 O^3, 3CO^2 + HO, CO^2.$$

The fact, that both the acid and neutral oxalo-sulphate of purpureocobalt contain two distinct acids, is also a very instructive one, since it completes the analogy between the polyacid bases and the polybasic acids. A polybasic acid, as, for example, tartaric acid, may unite with two different bases at once, and we now learn that a polyacid base may in like manner unite with two different acids. Thus we have

$$C^8 H^4 O^{10} \left\{ \begin{matrix} KO \\ NaO \end{matrix} \right., \quad 5NH^3 . Co^2 O^3 \left\{ \begin{matrix} SO^3 \\ C^2 O^3 \end{matrix} \right., \quad 5NH^3 . Co^2 O^3 \left\{ \begin{matrix} 2SO^3 \\ 2C^2 O^3 \end{matrix} \right..$$

The other point to which we refer, is the peculiarity in the constitution of xanthocobalt, in which one equivalent of oxygen in the secondary radical is not capable of replacement by chlorine, so that we have for the chloride of this base the formula

$$\overset{\frown}{NO^2} . 5\overset{\frown}{NH^3} . Co^2 O . Cl^2,$$

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while for the chloride of purpureocobalt we have

$$5NH^3.\overset{\frown}{Co^2}\,Cl.Cl^2,$$

and not, as we might expect from the analogy of xanthocobalt,

$$5NH^3.\overset{\frown}{Co^2}\,O.Cl^2.$$

The appearance of deutoxide of nitrogen as a conjunct is in itself well worthy of attention, and xanthocobalt forms, we believe, the only known instance in which this occurs. It seems *à priori* probable, that iridium and rhodium bases corresponding to xanthocobalt may be prepared by passing a current of NO^x into ammoniacal solutions of protosalts of those metals, or into solutions of Claus' bases, and we have already instituted experiments with these metals, the results of which we hope hereafter to communicate.

The theory which we have proposed for the ammonia-cobalt bases has also been brought forward by Claus, and applied to his rhodium and iridium compounds. Claus has extended the view in question to the ammonia compounds of metallic protoxides, and we conceive with advantage, in the case of those bases which contain more than one equivalent of ammonia, as for instance, the platinum, palladium, and iridium bases, having the formulæ

$$2NH^3.PtO \qquad 2NH^3.PdO \qquad 2NH^3.IrO.$$

The discovery of the biacid character of purpureocobalt and xanthocobalt, in connexion with the views which we have expressed with respect to the molecular structure of these bases, has led us to extend the theory of conjugation to the ammonia-platinum compounds. We consider these also as conjugate bases, and are of opinion that their constitution may be more simply expressed upon this than upon any other view yet proposed. The ammonia-platinum bases at present known are eight in number, of which two were discovered by Reiset, one by Gros, two by Raewsky, and three by Gerhardt. The empirical formulæ of these bases are as follows:—

Reiset's first base	$=N^2H^6PtO$	uniacid
„ second base	$=NH^3PtO$	„
Gros's base	$=N^2H^6PtClO$	„
Gerhardt's first base	$=NH^3PtO^2$	„
„ second base	$=N^2H^6PtO^2$	„
„ third „	$=NH^3PtClO$	„
Raewsky's first „	$=N^4H^{12}Pt^2ClO^5$	biacid
„ second „	$=N^4H^{12}Pt^2Cl^2O^4$	„

If we apply to these bases the results which we have obtained in the case of the ammonia-cobalt compounds, we may consider them as conjugates of platinum, chloride of platinum, and oxide of platinum, with 1 or 2 equivs. of ammonia, excepting Raewsky's bases, which may be regarded as containing a deutoxide of chlorine with 4 equivs. of ammonia. The formulæ of these bases become on this view—

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Reiset's second base	=	$NH^3.\overset{\frown}{Pt}.O$	uniacid
Gerhardt's first „	=	$NH^3.\overset{\frown}{PtO}.O$	„
„ third „	=	$NH^3.\overset{\frown}{PtCl}.O$	„
Reiset's first „	=	$2NH^3.\overset{\frown}{Pt}.O$	„
Gerhardt's second base	=	$2NH^3.\overset{\frown}{PtO}.O$	„
Gros's second base	=	$2NH^3.\overset{\frown}{PtCl}.O$	„
Raewsky's first „	=	$ClO^2.\overset{\frown}{4NH^3}.Pt^2O.O^2$	biacid
„ second base	=	$ClO^2.\overset{\frown}{4NH^3}.Pt^2Cl.O^2$	„

In comparing the formulæ of these bases with those of the ammonia-cobalt compounds, we remark several points of analogy. These are most striking in the case of Raewsky's two bases, which we consider analogous to xanthocobalt. Thus we have

Oxide of xanthocobalt	$NO^2.\overset{\frown}{5NH^3}.\overset{\frown}{Co^2}O.O^2$
Oxide of Raewsky's first base	$ClO^2.\overset{\frown}{4NH^3}.\overset{\frown}{Pt^2}O.O^2.$

Raewsky's second base contains chlorine in the radical in place of oxygen. We consider it, to say the least, very probable that there exists an analogous cobalt base having the formula

$$NO^2.\overset{\frown}{5NH^3}.\overset{\frown}{Co^2}Cl.O^2$$

like $ClO^2.\overset{\frown}{4NH^3}.\overset{\frown}{Pt^2}Cl.O^2$;

and we may here remark, that the compound which we have mentioned as one of the products of the action of a current of NO^x upon an ammoniacal solution of chloride of cobalt, appears to contain chlorine in the radical, since we have found this element in the dark brown-yellow oxalate which is thrown down by oxalate of ammonia from the solution.

The constitution of Gros's base becomes perfectly intelligible upon this view, as does that of the analogous base containing but 1 equiv. of ammonia. It can scarcely fail to escape notice that the theory of conjugates brings all the platinum bases under one point of view, and exhibits the analogy in their constitution in a very striking manner, by arranging them at once in three groups, of which the first two are exactly parallel. Thus we have for the radicals of the first six bases mentioned the formulæ—

$NH^3.\overset{\frown}{Pt}$	$2NH^3.\overset{\frown}{Pt}$
$NH^3.\overset{\frown}{PtO}$	$2NH^3.\overset{\frown}{PtO}$
$NH^3.\overset{\frown}{PtCl}$	$2NH^3.\overset{\frown}{PtCl},$

each uniting with a single equivalent of oxygen to form a uniacid base. The occurrence of a deutoxide of chlorine as a couplet is not more remarkable or more improbable than that of deutoxide of nitrogen; but experimental evidence is still wanting to support the view which we have taken of the constitution of Raewsky's bases,

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which have as yet been very imperfectly examined. Claus* has also applied the theory of conjugates to several of the ammonia-platinum bases, but has not considered the subject from precisely the point of view which we have taken, though his ideas, in the main, are the same. It is in the explanation of the difference in the saturating capacity of the various bases that Claus' view appears to us less satisfactory than that which we have proposed. It is scarcely necessary to remark that our theory applies to all bases containing ammonia and a metallic oxide. We may, however, observe that it also harmonizes perfectly with the ammonium theory if we consider ammonium as a conjugate hydrogen, or as represented by the formula $NH^3\overset{\frown}{.}H$.

We will here remark, that our view of the theoretical constitution of the ammonia-cobalt bases was distinctly enunciated in the paper already referred to, as published by one of ourselves, in 1851.

A glance at the formulæ of the ammonia-cobalt bases, suggests the possibility of generalizing the results which we have obtained, by two distinct methods. In the first place, it is evidently possible, theoretically at least, to replace one or more equivalents of ammonia in these compounds by an equal number of equivalents of a compound ammonia, as for example, by methylamine, ethylamine, &c. Thus there may be, for example, a species of roseocobalt, having the formula

$$5N(C^2H^3)^3\overset{\frown}{.}Co^2,$$

which would represent the base which we have described under that name, in which methylamine replaces ammonia. We have not yet been able to investigate this point with any degree of thoroughness, and will here only mention, that an experiment made by adding a solution of piperidine to one of chloride of cobalt, and allowing the solution to stand for some time in a half-filled flask, with frequent agitation, led to no decisive result. We selected piperidine for this experiment, because this alkaloid is comparatively easy to prepare, and does not itself oxidize by exposure to the air.

In the next place, the results of our investigation may be generalized by replacing cobalt by other metals. This, as we have already remarked, has been done by Claus, who obtained ammonia-rhodium and ammonia-iridium bases corresponding to roseocobalt, and like this, triacid bases. To judge, however, from the imperfect notices of Claus' papers which have hitherto reached us, his compounds are not isomorphous with those of roseocobalt.

We have ourselves made many experiments in this direction, though as yet without interesting results. Iron and manganese promised to afford similar classes of compounds, yet in their behaviour towards ammonia and oxygen the protosalts of these metals exhibit no analogy to those of cobalt. With chromium the case may be different, but we cannot as yet pronounce with certainty on this point. Experiments with nickel failed entirely, and yielded only ammonia-salts of the protoxide.

* Chem. Gazette, vol. xii. p. 441.

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The behaviour of ammoniacal solutions of protosalts of iron and manganese toward the mixture of gases, which we have denoted by the formula NO^x, is worthy of notice. When tartaric acid is added to a solution of protochloride of iron or manganese, and after the addition of a large excess of ammonia, a rapid current of NO^x is passed through the solution, the liquid soon becomes dark coloured, and after a time the whole of the iron or manganese is precipitated as a dark brown or nearly black flocky substance. The filtrate is free from the metal employed. No ammonia-iron or ammonia-manganese base is, however, formed under these circumstances.

In concluding for the present an investigation to which we have devoted our leisure for several years, and which has been one of extraordinary difficulty, we desire to state our conviction that the subject is by no means exhausted, but that on the contrary there is scarcely a single point which will not amply repay a more extended study. The number of bases which the sesquioxide of cobalt is capable of forming with ammonia is perhaps very large, and a careful study of the products of the decomposition of the salts of each base promises to yield an abundant harvest of interesting combinations. It is our hope to be able to return to the subject hereafter, and in a second part of our memoir to clear up some points which we have not as yet had time and opportunity fully to consider. In the mean time, we invite the attention of chemists to a class of salts which for beauty of form and colour, and for abstract theoretical interest, are almost unequalled either among organic or inorganic compounds.—Silliman's *American Journal for July* 1857.

Action of Nitromuriatic Acid upon Alcohol. *By* H. Bonnet.

The actions of nitric and muriatic acids upon alcohol have been investigated, and the resulting æthers are well known. The effect of nitromuriatic acid has not yet been studied.

$$NO^5 + HCl = NO^4 + HO + Cl$$

is the equation of nitromuriatic acid, and Gay-Lussac, by condensing the products of *aqua regia*, obtained the formula

$$NO^2\,Cl,\ NO^2\,Cl^2.$$

The following reactions are also known:—

$$C^4\,H^5\,O^2 + NO^5,\,HO = 2HO + \underbrace{C^4\,H^5\,O,\,NO^5}_{\text{Nitric æther.}}$$

$$C^4\,H^6\,O^2 + HCl = \underbrace{C^4\,H^5\,Cl}_{\text{Hydrochloric æther.}} + 2HO.$$

If commercial muriatic and nitric acids be employed, the products only differ by the equivalents of water.

The author mixed equal volumes of pure muriatic acid and monohydrated nitric acid in a test-glass with an equal volume of alcohol of spec. grav. 0·848, taking care to pour the *aqua regia* upon the alcohol. No action is observed at first; the liquid remains tranquil

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and no elevation of temperature takes place, but in from ten to fifteen minutes small bubbles are produced and the liquid becomes heated; the bubbles become more and more distinct, the liquid becomes turbid; the reaction grows very violent, and a spontaneous ebullition takes place, with evolution of penetrating vapours, which affect the eyes very disagreeably. The ebullition goes on for five or ten minutes; the liquid then cools by degrees and becomes bright green.

The distillation is effected in a retort with an adapter and with a receiver furnished with a tube, united by a caoutchouc tube with a U-tube, surrounded by a refrigerating mixture; then a second and third U-tube, the latter with one branch drawn out and not closed. The distillation takes place spontaneously. The products are aldehyde and nitric æther, formic æther and aldehyde, perhaps a compound of æthyle and a nitrous compound, chloral, and formic acid; perhaps also chloroform (?). The presence of hydrochloric æther was not ascertained. The gases evolved are a mixture of protoxide and deutoxide of nitrogen. By agitating the products of distillation with a little litharge and submitting them to fractional distillation, these products are recognized by their odours and different boiling-points.

The liquids remaining in the retort were distilled, and the presence of alcohol, acetic acid, acetic æther, oxalic æther, and acetal (?), or of an analogous body, which is volatile about 216° F., was recognized. The residue of the retort saturated with carbonate of lime furnished insoluble and soluble matters; namely, oxalate of lime, nitrate and chloride of lime, oxyglycolate of lime (?), and lastly, resinifiable matters of undetermined nature.

Theory may give as equations,—

$$C^4 H^6 O^2 + 2Cl = 2HCl + \underbrace{C^4 H^4 O^2}_{\text{Aldehyde.}}$$

$$C^4 H^6 O^2 + NO^5, HO = 2HO + \underbrace{C^4 H^5 O, NO^5}_{\text{Nitric æther.}}$$

$$\underbrace{C^4 H^4 O^2}_{\text{Aldehyde.}} + Cl^6 = 3HCl + \underbrace{C^4 HCl^3 O^2}_{\text{Chloral.}}$$

$$\underbrace{C^4 HCl^3 O^2}_{\text{Chloral.}} + 2HO = \underbrace{C^2 HCl^3}_{\text{Chloroform.}} + \underbrace{C^2 HO^2, HO}_{\text{Formic acid.}}$$

If there be, as may be supposed, a nitrous compound with the radical of alcohol, its equation would be

$$C^4 H^6 O^2 + NO^3, HO = 2HO + C^4 H^5 NO^4.$$

It would be a nitruret of æthyle.

The acetic and oxalic acids met with here, as elsewhere, in the products of distillation, should they still find alcohol, will give the corresponding æthers.—*Comptes Rendus*, Sept. 14, 1857, p. 386.

On the Tantalates. *By* H. Rose.

The solution of neutral tantalate of soda serves admirably for the production of other neutral tantalates. Solutions of the neutral

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salts of strong bases produce precipitates in it; and these are also neutral when the additions are not in excess. Tantalate of soda in this respect exhibits a different behaviour from the alkaline carbonates, borates, and silicates, which are not decomposed by other neutral salts into pure neutral compounds, but also form at the same time hydrates of the bases.

Solution of tantalate of soda does, however, produce precipitates consisting of acid tantalate of soda with the solutions of neutral alkaline salts, alkali being extracted from the tantalate in the solution even at ordinary temperatures. These precipitates are produced in the solution of tantalate of soda by solutions of the sulphates of potash and soda, the nitrates of potash and soda, and chlorides of potassium and sodium. The author shows that something of the same kind takes place in the solution of alkaline salts of other metallic acids, as for example in that of antimoniate of potash.

Tantalate of Ammonia.—Tantalic acid forms no neutral compounds with ammonia, but only acid salts, and even these cannot be produced directly by treating tantalic acid with liquid ammonia; they are formed by mixing solutions of the alkaline tantalates with ammoniacal salts. With tantalate of soda and muriate of ammonia a precipitate of the composition $NH^4O+9TaO^2+6HO$ is produced. Tantalate of potash, however, produces in a solution of muriate of ammonia a compound containing both potash and ammonia, the constitution of which may be expressed by

$$\left.\begin{matrix} KO \\ NH^4O \end{matrix}\right\} +10TaO^2+4HO.$$

Tantalate of Baryta.—The precipitate formed by tantalate of soda with chloride of barium has a composition which can only be determined with difficulty. Analysis, indeed, gave the composition $2BaO+3TaO^2+3HO$, but it is probable that the sulphate of baryta obtained still contained tantalic acid, and that the proportion of baryta to tantalic acid in the salt is as $BaO+2TaO^2$.

Tantalate of Magnesia.—Tantalate of soda mixed with an excess of sulphate of magnesia gives a compound which has exactly the composition $MgO+2TaO^2$. The salt contains $2\frac{1}{2}$ atoms of water, a quantity which also occurs in other tantalates.

Tantalate of Silver.—The precipitate formed by tantalate of soda with nitrate of silver is white. When dried in the air it is yellowish; when more strongly dried it becomes yellow, brown, and at 212° F. black; even after ignition the salt remains black. Its composition is $AgO+2TaO^2$; the amount of water stands in no simple relation to the oxide of silver, but it is probable that the salt loses some of its essential water at 212° F. By ignition it only loses its water; the oxide of silver is not reduced thereby, and is only deprived of its oxygen when heated in an atmosphere of hydrogen, when the tantalic acid remains unaltered. Tantalate of silver is completely soluble in ammonia.

Prototantalate of Mercury.—The precipitate of the salt is voluminous and of a greenish-yellow colour. By desiccation the salt is

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rendered chestnut-brown. Its composition is $Hg^2O + 2TaO^2$, and it contains 1 atom of water.

Perchloride of mercury produces no precipitate in a solution of tantalate of soda. If the solution contains an excess of soda, reddish-brown oxychloride of mercury is formed. But a gelatinous mass is never produced by perchloride of mercury in solutions of alkaline tantalates, by which the latter are essentially distinguished from the alkaline niobates and hyponiobates.,

By these carefully executed analyses of the neutral tantalates, the atomic composition of tantalic acid adopted by the author is completely confirmed.—*Bericht der Akad. der Wiss. zu Berlin*, 1857, p. 388.

Note on the Formation of Arsenite of Ammonia.
By M. V. DE LUYNES.

To obtain arsenious acid in a state of purity, Berzelius indicates the following process. The commercial acid is agitated for several hours at a temperature of 158° to 176° F. with ammonia in a closed vessel. The liquid is left standing for a few moments; and the limpid and hot portion is decanted into another bottle. On cooling, according to Berzelius, octahedric crystals of arsenious acid, containing no ammonia, are deposited.

In repeating this process the author obtained an abundant deposit of crystals, but as they presented by no means the properties of arsenious acid, he examined them carefully. When left in contact with the mother-liquor in an open vessel, the crystals gradually dissolved, and at last disappeared entirely. The ammonia was evolved slowly in the air. After some time the liquid had no longer the least ammoniacal odour, although possessing a strongly alkaline reaction. After the lapse of a sufficiently long time, a second deposit was formed, of crystals less transparent than the former, and of an octahedral form. This was pure arsenious acid containing no ammonia.

The experiment was recommenced, setting aside the crystals first formed. These were well-defined prismatic needles, amongst which no octahedra could be seen. They had a strong ammoniacal odour. After being left to drain for a few moments upon unglazed porcelain, they were rapidly dried between paper and analysed. They contained—

Water	8·67
Ammonia	13·40
Arsenious acid	77·93

Arsenite of ammonia contains—

Water	7·20
Ammonia	13·60
Arsenious acid	79·20

These crystals therefore are arsenite of ammonia. This salt according to Pasteur, decomposes rapidly in the air. This is the reason of the excess of water and loss of ammonia in the above analysis.

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The first crystals deposited being arsenite of ammonia, their solution in the mother-liquor is easily explained. Arsenite of ammonia is much more soluble in pure water than in ammonia. The water losing its gas in contact with the air, the solubility of the salt increases; then the ammonia being completely evolved, there only remains a solution of arsenite of ammonia which is decomposed slowly in the air, and gives origin to a deposit of octahedral arsenious acid.—*Comptes Rendus*, June 29, 1857, p. 1353.

Note on the Subsulphuret of Carbon, CS. *By* E. BAUDRIMONT.

It is well known that there is a sulphuret of carbon, CS^2, corresponding with carbonic acid, CO^2, but we have hitherto been unacquainted with the subsulphuret of carbon, CS, corresponding with carbonic oxide, CO. This compound the author has discovered. It is obtained:—

1. By decomposing the vapour of ordinary sulphuret of carbon. CS^2, by spongy platinum or pumice-stone heated to redness; under these circumstances CS^2 is decomposed into an abundant deposit of sulphur and a gaseous body, which is the subsulphuret CS;
2. It is also obtained in the preparation of the liquid sulphuret CS^2, and simultaneously with the latter;
3. By the decomposition of the vapours of CS^2 at a red heat by means of pure lamp-black, wood charcoal, and especially animal charcoal in fragments;
4. By the decomposition at a red heat of the vapours of CS^2 by hydrogen;
5. By the calcination of sulphuret of antimony with an excess of charcoal;
6. By the reaction of carbonic oxide upon sulphuretted hydrogen at a red heat,

$$CO + HS = HO + CS;$$

7. By the reaction of sulphurous acid upon bicarburretted hydrogen at a red heat;
8. By that of bicarburretted hydrogen upon chloride of sulphur at a red heat;
9. During the decomposition of sulphocyanogen by heat, &c.

The first process furnishes this gas tolerably pure; the others mixed with suphuretted hydrogen and carbonic oxide gas. It is purified by being passed rapidly through solutions of acetate of lead and protochloride of copper dissolved in muriatic acid; it is then dried and collected over mercury.

It is gaseous, colourless, and endowed with an odour which resembles that of ordinary sulphuret of carbon, but not disagreeable and strongly ætherial. When breathed in too large a quantity, it appears to be powerfully anæsthetic. It burns with a fine blue flame, producing carbonic and sulphurous acids, and a little sulphur. Its density is a little greater than that of carbonic acid. It resists the cold of a mixture of ice and salt. Water dissolves nearly its

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volume of it, but decomposes it rather rapidly into sulphuretted hydrogen and oxide of carbon,—

$$HO + CS = CO + HS.$$

It is scarcely more soluble in alcohol or æther. Solution of protochloride of copper does not absorb it. Solution of acetate of lead is not immediately blackened by it, but after several hours of contact the liquid becomes black, and after several days the salt is completely converted into oxide of carbon and sulphuret of lead. In contact with alkaline solutions of potash, soda, &c., its decomposition is rapid. With lime-water it gives sulphuret of calcium and a volume of oxide of carbon equal to that of the gas employed. This remarkable reaction clearly establishes its composition,—

$$CaO + CS = CaS + CO.$$

No carbonate of lime is produced. At a red heat it is slightly decomposed,—1. by spongy platinum; 2. by aqueous vapour into HS and CO; 3. more readily by hydrogen into HS and a carburretted hydrogen; 4. entirely by copper into graphitoid carbon and sulphuret of copper; 5. when exposed to the sun with its volume of chlorine, there is a reaction, partial condensation, and formation of products which the author is now investigating.

When exploded with oxygen in the eudiometer, it gives equal volumes of carbonic and sulphurous acids, whence its composition is CS. The same conclusion is arrived at from the determination of the quantities of carbon and sulphuret of copper furnished by its reaction upon this metal.—*Comptes Rendus*, May 11, 1857, p. 1000.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On Dyeing Silk, Wool, and Cotton with Murexide.

If uric acid be treated with nitric acid which has been diluted with an equal volume of water, it dissolves with the aid of a gentle heat in this oxidizing agent. If this solution be carefully evaporated to dryness, an intensely red mass is obtained, which acquires a dark, purple-red shade, when it is treated with ammonia. This reaction is so striking and certain, that it has already been long employed by chemists for the detection of uric acid in organic substances. In the year 1818, Prout found that this substance is composed of ammonia and a peculiar body, which exhibits the properties of an acid. He describes the preparation of this acid in the following way:—Pure uric acid is digested with dilute nitric acid; it is dissolved with strong effervescence. The excess of nitric acid is then neutralized with ammonia, and the whole is carefully evaporated. During the evaporation the colour of the solution changes, it gradually becomes purple-red, and numerous dark red, granular crystals, which sometimes appear greenish on the surface, are precipitated from it. These crystals consist of ammonia and the acid under consideration.

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Purpurate of Ammonia (Murexide), crystallizes in four-sided prisms, which appear transparent and intensely garnet-red, with remarkably beautiful green reflexions. The latter phænomenon is also observed more or less on the other alkaline salts, and even on those of the alkaline earths. Purpurate of ammonia dissolves in about 1500 parts of water at 59° F.; boiling water dissolves considerably more of it. The solution has a fine carmine or rose-red colour. It is insoluble, or but slightly soluble in alcohol and æther. If the solutions of the neutral salts of other bases be mixed with the aqueous solution of purpurate of ammonia, a number of other purpurates are obtained.

Purpurate of Lime.—If saturated boiling solutions of purpurate of ammonia and chloride of calcium be mixed together, a pulverulent precipitate of purpurate of lime is obtained; it has the colour of the raw lobster. It is but slightly soluble in cold water, but more so in boiling water; the solution possesses a beautiful purple-red colour.

Purpurate of Mercury.—Perchloride of mercury produces a fine purple-red precipitate in the solution of purpurate of ammonia; the solution entirely loses its colour.

Purpurate of Lead.—If solutions of purpurate of ammonia and nitrate of lead be mixed together, the fluid becomes rose-red, but furnishes no precipitate.

Purpurate of Zinc.—A solution of acetate of zinc gives a golden yellow precipitate with purpurate of ammonia, and on the surface of the fluid very shining, iridescent films, in which green and yellow colours predominate, are formed.

These compounds of purpuric acid have been already described by Prout. Their beautiful colours furnish a sufficiently characteristic token to distinguish them from all other substances. Prout also stated that some purpurates, for example purpurate of lime, may be employed in painting, and he also recommended their use for dyeing wool and other materials of animal origin.

From this we see that Prout had only to carry out these beautiful experiments of his on a large scale, and to introduce them into the arts, in order to have arrived at the same point, to which we have only come forty years later. The high price of uric acid at that time (it cost 150 to 200 francs the kilogrm., whereas now it is only 10 francs) has been the principal cause of its remaining unapplied to technical purposes.

The denomination *murexide*, chosen by Liebig and Wöhler, for the purpurate of ammonia, has repeatedly led to the opinion that it was identical with the Tyrian purple of the ancients, *Murex* being the name of the Mollusk which is said to have furnished that dye; but the purple of the ancients resists the action of the strongest acids, whereas murexide is attacked by the weakest, and also by a number of other reagents, which have no action upon most dye-stuffs. The investigations of Prout showed that murexide, which has little or no colour of itself, may furnish lake-colours of various tones and nature in combination with different bases. After this

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it will not be surprising that the experiments made by Schlumberger and others upon this subject turned out failures, as they directed all their endeavours to the production of murexide by the aid of heat upon the tissues; now murexide is nothing but purpurate of ammonia, and we have therefore no prospect of producing a firm union of it with the fibres.

Dyeing of Silk and Wool, by Depoully.—Two years ago Depoully succeeded in dyeing silk and wool with murexide. The process is very simple and beautiful for silk; for wool, however, it still leaves much to be desired.

To dye silk, a solution of murexide is mixed with a certain quantity of a solution of perchloride of mercury. These two fluids only become turbid after the lapse of a certain time, so that silk may be dipped into them, when it immediately becomes of a purple-red colour. The intensity of the colour depends upon the concentration of the fluid and the quantities of each solution that have been employed.

With wool the process is not so simple; an acid, such as oxalic acid, must be made use of to produce the colour. The process which has given the best results in dyeing wool red with murexide, is as follows:—The wool is well-washed and rinsed, and then immersed for a certain time in a concentrated bath of murexide, wrung out, and dried in the air. It is then put into a bath composed of

60 grms. of perchloride of mercury and
75 grms. of acetate of soda,
to 10 litres of water.

The bath must have a temperature of 104° to 122° F.

Dyeing Cotton, by Lauth.—The dyeing of cotton, linen, and, in short, tissues of every kind by means of murexide, has been rendered very simple by the fortunate discoveries of Lauth. The process consists in fixing oxide of lead upon the cotton, either by immersing it first in a bath of acetate of lead, and afterwards in one of liquid ammonia, or by putting it directly into a tub with oxide of lead and lime (plumbate of lime). In either way, a union of the fibres with oxide of lead is obtained, and all that remains is to produce the colour by putting the stuff into a bath of pernitrate or perchloride of mercury, or of a mixture of the two, with the addition of a certain quantity of acetate of soda.

To print this colour, sufficiently thickened nitrate of lead is mixed with as much murexide as is necessary to produce the desired shade; the stuff is then dried and put into a bath of

100 litres of water,
1 kilogrm. of perchloride of mercury,
1 kilogrm. of acetate of soda.

In this way beautifully coloured prints are obtained, but only on a white ground.—Dingler's *Polyt. Journal*, cxlv. p. 137.

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Simple Process for rendering Stuffs Waterpooof.

M. Thieux, of Marseilles, proposes the following simple process for rendering stuffs water-proof.

In two vessels, each of a content of 12 gallons of river water are dissolved, in the one $3\frac{1}{5}$lbs. of alum, in the other the same weight of sugar of lead. When the solutions are complete, pour the liquids together, by which will be formed an insoluble sulphate of lead, and soluble acetates of alumina and potassa, mixed with a slight excess of alum. As soon as the liquid has become clear, it is drawn off and the stuffs plunged into it; they must be strongly compressed while under the liquid to expel the air from their pores, and then suffered to soak for at least four hours, so as to insure the perfect penetration of the liquid everywhere. When withdrawn they are lightly shaken, then dried, brushed, and pressed with a hot iron. It appears that various specimens of cloth experimented on by the Committee, absorbed from 11 to 17 per cent. of their weight of saline matters, and retained their original appearance, and their pliability at all temperatures. But after immersion in fresh water for 24 hours, they lost all their additional weight. As to the efficacy in this process, there appears to be a very serious difference of opinion; the conclusions of the Committee appointed to examine it, as reported by M. Jacquelain, are that it is not new, nor as good as was announced; but it had been tried and approved for five years by the Lyons and Mediterranean Railroad Company; that the Committee could not tell whether it was durable or not: its cost was about 20 cents for water-proofing a coat or pair of pantaloons. On the other hand, M. Balard, known to all as one of the most distinguished and careful chemists of France, reports that the thinnest woollen cloths impregnated with it, are totally impermeable to water after weeks of contact with it; that the water evaporates from them and does not pass through; that cloths which had been soaked for 48 hours in fresh water, were as impermeable afterwards as before; that cloths rendered water-proof in this way, and exposed on wicker-frames to the rains of October, never allowed a drop of water to pass; that a cloak of cloth thus prepared, stretched over a willow frame, and exposed to the stream from a fire-engine worked by six strong men, from a distance of 15 yards, allowed no water to pass, except where the stuff was in contact with the frame and was compressed upon it by the violence of the jet, but the transpiration from the skin appears to destroy the impermeability, so that it is probably applicable only to exterior clothing; finally, that there is every probability that it is lasting, as appears from the certificates. M. Balard himself testifies that an overcoat worn by him for five months, which had been beaten and rubbed and subjected to all the ordinary usage of overcoats, remained perfectly impermeable. Clothes prepared in this way are said to be softer to the touch, warmer, absorbing less moisture, drying more quickly, and therefore more durable.

It would appear, therefore, that this process, which is cheap and easily applicable, even after articles are made up, is well worth experimenting upon.—*Journ. of the Franklin Inst.* for April 1857.

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On the so-called Bronze Colours. *By* C. R. König.

The author has analysed eight different bronze colours, the so-called bronze powders of commerce. These colours, which now form no inconsiderable article of commerce, are prepared by beating out bronze into thin leaves like gold leaf, and triturating these with water upon stones, the water being mixed with some thickening agent such as honey. The samples examined are marked with the numbers which they bear in commerce. They are the following:—

Indication of the bronze in commerce.	Copper.	Zinc.	Iron.	Tin.	Observations.
1. Pale yellow	82·33	16·69	0·16	...	Has a speis-yellow colour.
2. Bright yellow	84·5	15·3	0·07	...	Fine gold colour. [tinge.
3. Reddish-yellow	90·0	9·6	0·20	...	Brassy yellow with a reddish
4. Orange	98·93	0·73	0·08	...	Colour of tarnished bright copper. [purple.
5. Copper-red	99·90	...	trace	...	Copper-red with a tinge of
6. Violet	98·22	0·5	0·3	trace	Purplish-violet colour.
7. Green	84·32	15·02	0·03	trace	Pale bluish-green.
8. White	...	2·39	0·56	96·46	Tin-white to lead-gray.

It appears that several of these bronzes with the most different tints possess a very similar composition.

The author soon convinced himself that the tints are produced by ignition; they are so-called tarnish-colours, which have been given to these powders by burning. All these bronzes contained a small amount of fatty matter, which is greater in the English than in the German samples, and this fat is certainly added intentionally, in order to attain a uniform and low temperature in the superficial oxidation of the bronzes. One-half per cent. of wax and paraffine added to the powder and heated with it with stirring, is sufficient to attain the object with certainty.

The author also refers to the so-called *iron-black*, with which a colour like that of clean gray cast iron is given to plaster figures. It consists of very finely-divided antimony, which may be obtained by precipitating solutions of antimony by means of zinc.—*Journ. für Prakt. Chem.*, lxix. p. 461.

Green Varnish.

For the production of this varnish, a resinous soap must first be prepared, which is easily done by the following recipe:—15 parts by weight of powdered colophony are stirred up with 18 parts by weight of water in an iron pot, and heated to boiling; a solution of 2 parts of crystallized carbonate of soda in 5 parts of water is then slowly added, by stirring, to the mixture, which is again brought to boil. After the addition of a similar quantity of carbonate of soda, the whole is boiled until all the resin has disappeared; it is then allowed to cool, and to become clear by standing. The clear solution is mixed with an aqueous solution of sulphate of copper, as long as a precipitate is produced; this is then allowed to settle, or filtered through linen. After drying, it forms a pale green, pulverulent mass, which dissolves readily in turpentine, and then forms a beautiful green varnish.—*Polyt. Centralbl.* 1857, p. 544.

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THE CHEMICAL GAZETTE.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Connexion of the Aldehydes with the Biatomic Alcohols.

By A. ENGELHARDT.

Löwig and Erdmann in 1839 and 1840 investigated the action of chloride of æthylene ($C^4 H^4 Cl^2$) upon sulphuret of potassium and hydrosulphide of sulphuret of potassium, when they obtained

$C^4 H^4 S^2$, sulphuret of æthylene,
$C^4 H^6 S^4$, hydrosulphide of sulphuret of æthylene.

In 1855, E. Meyer and H. Buff, independently of each other, obtained

$C^4 H^4, 2C^2 NS^2$, sulphocyanide of æthylene,

by the action of chloride of æthylene upon sulphocyanide of potassium.

Not long since Wurtz obtained

$$\left.\begin{matrix} C^4 H^4 \\ C^4 H^3 O^2 \\ C^4 H^3 O^2 \end{matrix}\right\} O^4, \text{ biacetate of glycol,}$$

by the action of iodide of æthylene upon acetate of silver, and from this by the action of caustic potash, he obtained

$$\left.\begin{matrix} C^4 H^4 \\ H^2 \end{matrix}\right\} O^4, \text{ glycol.}$$

The explanation of the chemical import, as also of the relations of the above compounds to each other, is undoubtedly due to Wurtz, who showed that the compounds $C^n H^n Cl^2$ in general are chlorides of the diatomic group $C^n H^n$ (which replace 2 atoms of hydrogen), and that they are also related to the biatomic alcohols, $C^n H^{n+2} O^4$, discovered by him, in the same way as the chlorine compounds of æthyle, $C^4 H^5 Cl$, to alcohol, $C^4 H^6 O^2$.

As a general rule, the mutual relations of the monoatomic, diatomic, and triatomic alcohols, and the bodies derived from these (the chlorine, sulphur, nitrogen, and similar compounds of these alcohols), are the same as those of the monobasic, bibasic, and tribasic acids.

Just as the bibasic acids correspond with the anhydrides which are related to them as follows,—

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$$H^2O^2 \qquad \left.\begin{matrix}H^2\\H^2\end{matrix}\right\}O^4$$

$$S^2O^4, O^2 \qquad \left.\begin{matrix}S^2O^4\\H^2\end{matrix}\right\}O^4,$$

the diatomic alcohols must have corresponding anhydrides, which are the aldehydes now known to us.

Ordinary aldehyde is actually $(C^4H^4)O^2$ (of the type H^2O^2), and stands in the same relation to glycol, $C^4H^6O^4$ (type H^4O^4), as the anhydride of succinic acid to succinic acid itself, or as the anhydrous to the hydrated oxide; if such a relation really exists, we ought to obtain from the aldehydes the chlorides $C^nH^nCl^2$, for example, by the action of pentachloride of phosphorus.

For his first investigation the author selected benzoic aldehyde, from which Cahours had previously obtained the compound $C^{14}H^6Cl^2$, which he called chlorobenzole, by the action of pentachloride of phosphorus. The author investigated the action of chlorobenzole upon silver salts, and by this means obtained from chlorobenzole and benzoate of silver a neutral compound of the composition $C^{42}H^{16}O^8$:—

$$2\left(\left.\begin{matrix}C^{14}H^5O^2\\Ag\end{matrix}\right\}O^2\right)+C^{14}H^6,Cl^2=\left.\begin{matrix}C^{14}H^5O^2\\C^{14}H^5O^2\\C^{14}H^6\end{matrix}\right\}O^4+2AgCl.$$

To prepare chlorobenzole the author proceeded as follows:—

A weighed quantity of pentachloride of phosphorus was put into a retort; a weighed (atomic) quantity of oil of bitter almonds, previously purified by peroxide of mercury and distillation, was then very gradually poured in through the neck of the retort by means of a funnel. A violent reaction took place, and the whole mass was converted into a slightly coloured fluid. This was distilled off, when a carbonaceous residue remained in the retort; in the receiver a distillate collected, from which some pentachloride of phosphorus always separated, because an excess of this had been taken, in order to attain a complete decomposition of the oil of bitter almonds. The colourless transparent distillate was distilled at 230°—248° F., to separate oxychloride of phosphorus, but the residuary fluid was treated first with water, then with caustic potash, washed with water, dried over chloride of calcium, and distilled. The chlorobenzole poured away from the chloride of calcium exhibited a constant boiling-point of 388° F., and gave a perfectly clear and colourless distillate, which however always contained muriatic acid. For this reason, when perfectly pure chlorobenzole is to be employed (as, for example, for its action upon benzoate of silver), the distillate is to be agitated with litharge, which immediately takes up the muriatic acid.

By the action of chlorobenzole upon an alcoholic solution of hydrosulphide of sulphuret of potassium, Cahours obtained sulphobenzole ($C^{14}H^6, S^2$) in the form of white, shining scales.

Buff also tried the action of chlorobenzole upon an alcoholic solution of hydrosulphide of sulphuret of potassium, and obtained chlo-

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ride of potassium and an oleaginous mass, which he could not purify. The author obtained the same results as Cahours; when chlorobenzole is heated with an alcoholic solution of $(KH)S^2$, a violent reaction takes place, chloride of potassium and an oleaginous body separate, and by treatment with water, KCl is dissolved and the oleaginous body remains behind. This sometimes does not solidify for a long time, but when it is dissolved in strong boiling alcohol, the fluid solidifies completely on cooling, forming a mass of white, shining scales, exactly as described by Cahours.

By the action of nitric acid upon the sulphur compound obtained by him, Buff obtained no acid; but Cahours obtained, by the action of nitric acid upon sulphobenzole, a crystalline body which dissolves in alkalies. The author obtained the same result as Cahours; the crystalline body dissolves in carbonate of soda and ammonia, and is precipitated from these solutions by acids.

In treating chlorobenzole with caustic potash, in order to purify it, the author has constantly observed that the solution of caustic potash when poured away, which possesses the odour of chlorobenzole, in course of time acquires that of oil of bitter almonds; this is due to the decomposition of the chlorobenzole by caustic potash. The following experiment shows that even water gradually decomposes chlorobenzole. A small quantity of chlorobenzole was washed with water until the latter no longer exhibited an acid reaction; water was then poured over it, and the whole was left to stand for some days, when the water standing over the chlorobenzole had acquired an acid reaction, gave a precipitate with nitrate of silver, and smelled like bitter almonds. After the evaporation of this water in the air, an acid is obtained, which crystallizes in shining needles and resembles benzoic acid. In this case chlorobenzole is decomposed by water, and furnishes HCl and $C^{14} H^6 O^2$, which dissolves in water, becomes oxidized in the air during evaporation and converted into $C^{14} H^6 O^4$.

According to Gerhardt's observations, the oxides of silver and mercury decompose chlorobenzole and furnish chloride of mercury or silver, and oil of bitter almonds. Oxide of lead, left for a long time in contact with chlorobenzole, decomposes it and forms chloride of lead.

Aqueous ammonia has scarcely any action upon chlorobenzole, at least a mixture of chlorobenzole with strong ammonia which stood for more than two months, underwent very little change. Buff says that an alcoholic solution of ammonia acts upon chlorobenzole, and that muriate of ammonia is formed; he does not, however, say what becomes of the organic group.

There are also some amide compounds of the biatomic group, $C^{14} H^6$, which replaces 2 atoms of hydrogen:—

Hydrobenzamide is probably $N^2 \left\{ \begin{matrix} C^{14} H^6 \\ C^{14} H^6 \\ C^{14} H^6 \end{matrix} \right.$

Benzoylanilide is probably $N \left\{ \begin{matrix} C^{14} H^6 \\ C^{12} H^5. \end{matrix} \right.$

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Chlorobenzole acts as follows upon sulphocyanide of potassium. When alcoholic solutions of sulphocyanide of potassium and chlorobenzole are mixed together and heated, chloride of potassium separates, and the fluid, when diluted with water, furnishes a brown oil, which the author could not purify for analysis. Buff obtained the same result.

Chlorobenzole acts very energetically upon the silver salts of organic acids.

1. *Chlorobenzole and Benzoate of Silver.*—When benzoate of silver (2 atoms) is mixed with chlorobenzole (1 atom) in a flask, and the flask is strongly shaken, a reaction takes place very rapidly, accompanied by a considerable evolution of heat (to lessen the reaction, the flask is put into cold water); chloride of silver is formed, together with a yellowish oil, which solidifies into a white tallowy mass. After the completion of the reaction, the flask is heated in the water-bath to 176° F., and the mass obtained is treated with æther when it has cooled. The ætherial solution furnished a yellowish-white crystalline mass after evaporation, consisting of benzoic acid, benzoate of benzole, and a small quantity of a volatile body. The mass had a penetrating odour, resembling that of chlorobenzole; it lost weight when exposed to the air over sulphuric acid.

When this crystalline mass is treated with a small quantity of alcohol, a fluid oil is obtained, of which a portion remains in the alcohol and is thrown down by water. The crystalline mass, when dissolved in alcohol, was treated with a solution of carbonate of soda, when an oil was deposited; sometimes the mass was treated directly with a solution of carbonate of soda, when an oleaginous mass, insoluble in that fluid, was also obtained. The product obtained after treatment with carbonate of soda, was dissolved in æther, after the evaporation of which it formed a yellowish oil. This oil solidified in course of time, and when it is dissolved in alcohol and left to evaporate spontaneously, crystals are obtained.

The neutral product, insoluble in carbonate of soda, obtained in this way by the action of chlorobenzole upon benzoate of silver, is, as shown by the following analyses, bibenzoate of benzole ($C^{42}H^{16}O^8$), and the reaction is thus expressed:—

$$\underset{\text{Chlorobenzole.}}{C^{14}H^6Cl^2} + 2\left\{\underset{\text{Benzoate of silver.}}{\left.\begin{matrix}C^{14}H^5O^2\\Ag\end{matrix}\right\}O^2}\right\} = \left.\begin{matrix}C^{14}H^5O^2\\C^{14}H^5O^2\\C^{14}H^6\end{matrix}\right\}\underset{\text{Bibenzoate of benzole.}}{O^4} + 2AgCl.$$

The analyses gave—

C	75·14	74·40	75·72	76·08	75·90	75·68	42 = 252		75·90
H	4·82	4·98	5·23	5·48	5·30	4·74	16	16	4·82
O	...	...	...	...	...	...	8	64	19·28

Bibenzoate of benzole dissolves readily in æther, after the evaporation of which it is obtained in the form of a yellowish oil. In the air this oil solidifies after some time to form a solid white mass, which fuses at 122° F.; when more strongly heated, it is decomposed. It is much less soluble in alcohol than in æther; the hot alcoholic solution becomes turbid and deposits an oil, which, in

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course of time, becomes converted into a crystalline mass. By the slow evaporation of the solution of benzoate of benzole in alcohol, or what is better in alcohol and æther, transparent crystals are obtained, which have no odour when they are pure. It is insoluble in water, and also in an aqueous solution of ammonia; in concentrated sulphuric acid it dissolves with a brown colour. In nitric acid it dissolves when heated, with evolution of brown fumes; the solution, on cooling, furnishes a solid white body. When heated with a strong aqueous solution of caustic potash, the bibenzoate of benzole first of all dissolves, but afterwards decomposes, and the solution solidifies on cooling into a crystalline mass which is soluble in an excess of water; with weak sulphuric acid the solution gives a white precipitate, which is difficult of solution in water, but does not resemble benzoic acid. The author has not yet examined these products; but he has remarked no alcohol insoluble in potash is formed.

To purify the bibenzoate of benzole, the crystalline mass extracted by æther from the product of the action of chlorobenzole upon benzoate of silver was treated with carbonate of soda. The carbonate of soda then extracts from it a pretty large quantity of acid, which proved to be benzoic acid. The acid was thrown down from the solution in carbonate of soda by weak sulphuric acid, then well washed and converted into a baryta salt. Result, 36·08 and 36·12 per cent. of barium.

2. *Chlorobenzole and Acetate of Silver.*—Chlorobenzole acts upon acetate of silver when heated; the reaction is very strong, and furnishes chloride of silver and a fluid oleaginous product. The mass was extracted with æther, and the ætherial solution, after the evaporation of the æther, gave a yellowish oil, which, when left for some time in a little flask, produced on its walls a coating of small, fine prismatic needles. To remove the chlorobenzole completely, the oil obtained was again heated with a small quantity of acetate of silver, and then extracted with æther; the ætherial solution, when evaporated in the air, furnished an oleaginous product, in which acicular crystals of an acid, resembling benzoic acid, were formed. This product was treated with carbonate of soda, which dissolved the crystalline needles; the remaining oil was extracted with æther, after the evaporation of which the remaining oleaginous product, when left standing in the air in a small dish, again gave crystalline needles resembling the former. This circumstance did not permit this product to be analysed; but after it had been again treated with carbonate of soda, the author tried the action of caustic potash upon it. When heated with a strong aqueous solution of potash, the oleaginous product is decomposed; after cooling, a white crystalline mass is formed which is soluble in water, and, on the addition of sulphuric acid, produces acetic acid and a white precipitate, which is but slightly soluble in water. The oleaginous product is probably

$$\text{Biacetate of benzole } \left.\begin{matrix} C^4 H^3 O^2 \\ C^4 H^3 O^2 \\ C^{14} H^6 \end{matrix}\right\} O^4,$$

which of course requires further confirmation.

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Chlorobenzole also acts very energetically upon succinate of silver.

The following Table represents the compounds of the biatomic group $C^{14} H^6$, which replaces H^2:—

Oxide.....	$(C^{14} H^6) O^2$, oil of bitter almonds.
Alcohol.....	$\left.\begin{matrix} C^{14} H^6 \\ H^2 \end{matrix}\right\} O^2$, unknown.
Sulphur compound ..	$(C^{14} H^6) S^2$, sulphobenzole.
Chlorine compound ..	$(C^{14} H^6) Cl^2$, chlorobenzole.
Benzoate of benzole ..	$\left.\begin{matrix} C^{14} H^5 O^2 \\ C^{14} H^5 O^2 \\ C^{14} H^6 \end{matrix}\right\} O^4$.
Amide	$\left.\begin{matrix} (C^{14} H^6) \\ (C^{14} H^6) \\ (C^{14} H^6) \end{matrix}\right\} N^2$, hydrobenzamide.

The formation of these compounds would be more difficult to explain, if benzoic aldehyde be regarded as

$$\left.\begin{matrix} C^{14} H^5 O^2 \\ H \end{matrix}\right\}, \text{ or as } \left.\begin{matrix} C^{14} H^5 \\ H \end{matrix}\right\} O^2.$$

As cuminic aldehyde is homologous with benzoic aldehyde, chlorocumole will probably act upon silver salts in the same way as chlorobenzole. Tütschef is at present occupied with the investigation of this subject.—*Bull. de St. Pétersb.* xvi. p. 50.

On some little-known Reactions of Boracic Acid and the Borates. By C. Tissier.

In 1854 the author described the solvent action exerted by a boiling solution of boracic acid upon certain insoluble oxides, at the moment of their precipitation. In the present memoir he furnishes some further details upon this subject, and also upon the solvent action of boracic acid upon the metallic sulphurets which are decomposable by weak acids.

In a neutral solution of the metallic salt to be experimented on, a quantity of crystallized boracic acid, equal to fifteen or twenty times the weight of the salt, is dissolved; a quantity of borax just sufficient to saturate the acid of the salt is then added, so that the oxide is precipitated if it is not soluble in boracic acid.

The metallic sulphurets experimented on were those capable of being dissolved by dilute acids, such as those of manganese, iron, cobalt, nickel, zinc, and cadmium. The mode of experimentation is the same as for the oxides; it consists in preparing a solution containing—1, the metallic salt as neutral as possible; 2, an excess of boracic acid sufficient to prevent any precipitation in case the sulphuret should be capable of redissolving; and 3, a quantity of borax sufficient to neutralize the acid of the salt. The liquid thus prepared is boiled, and a rapid current of sulphuretted hydrogen, produced by the action of sulphuret of antimony and muriatic acid, is passed through it. From the facts obtained it appears,—

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1. That a boiling solution of boracic acid is capable of dissolving the protoxides of calcium, magnesium, manganese, iron, cobalt, nickel, zinc, and cadmium.

2. That it cannot dissolve the protoxides of lead, copper, and tin, any more than the sesquioxides of aluminium, chromium, and iron.

Boracic acid is therefore capable of dissolving the protoxides of all the metals which decompose water in the presence of acids, and has no action upon the protoxides of the other metals, or upon the higher oxides, as the sesquioxides and binoxides.

Of the insoluble metallic sulphurets, boracic acid only dissolves one, namely sulphuret of manganese; this fact may be available in analysis for separating manganese from all other metals, especially zinc, nickel, and cobalt.—*Comptes Rendus*, Sept. 21, 1857, p. 411.

On some Soluble Basic Salts of Tin. *By* JOHN M. ORDWAY.

Some years ago a singular liquid came to my notice, in the course of my business, under the strange sounding but appropriate name of nitrate of tin; and while seeking to determine its nature, some things were observed that are unexplained in systematic treatises on chemistry. But some properties since shown to belong to the salts of alumina have been found, by further experiments, to be possessed also by certain combinations of tin.

It is well known that when we attempt to dissolve tin directly in pure nitric acid, the metal is simply changed to insoluble stannic acid, nitric oxide being given off. To be sure, if feathered tin is put into very weak nitric acid, say of specific gravity 1·15, a small quantity is quietly taken up, but in a short time it is thrown down again as a white powder containing no nitric acid. If, however, a very little hydrochlorate of ammonia is first added to the dilute acid, the reaction is different; nitrous oxide is given off and the metal remains permanently in solution. A small proportion of hydrochloric acid answers the same purpose as the ammonia salt, since the first portions of tin added deoxidize a portion of nitric acid and ammonia is formed, according to a well known reaction. Indeed, as circumstances vary, we may have the formation of ammonia, the evolution of nitrous oxide, or the disengagement of nitric oxide; and often all three phænomena occur in the same experiment*.

It is not easy to determine whether the presence of ammonia is essential to prevent the formation of stannic acid, for we cannot keep it out. We might infer that nitrate of ammonia would answer instead of the muriate, but such I have not found to be the case. It seems more probable that the hydrochloric acid is what exerts the needed influence.

The nitrate of tin before mentioned, was made by dissolving

* The same, as is well known, is partially true of some other metals. Thus I have observed in making nitrate of lead in the large way, that nitric acid of spec. grav. 1·14 dissolves lead rapidly, giving off protoxide of nitrogen almost pure, while a stronger acid acts more slowly, and nitric oxide is evolved.

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1 equiv. of sal-ammoniac in 9 of nitric acid of spec. grav. 1·16, and dropping in gradually 6 equivs. of tin. It can be made right only in cool weather. It is a brown liquid which behaves with most reagents like the protosalts of tin, and but for its colour we might take it to be merely a protonitrate. But by operating with a stronger nitric acid mixed with a large proportion of muriatic acid, we may push the matter a great deal further and get entirely beyond the reach of such a supposition.

In repeating former trials, experiments have recently been made with nitric acid of spec. grav. 1·39, and muriatic acid of spec. grav. 1·16, mixed in various proportions. In one case equal parts of each acid took up tin enough to make a liquid of spec. grav. 2·24, having about the colour and consistence of molasses. Analysis showed this solution to contain about 24 equivs. of tin to 3 equivs. of nitric acid, 6 equivs. of hydrochloric acid, and 2 equivs. of hydrochlorate of ammonia.

Here we have 8 equivs. of tin retained in solution by 3 of acid.

Another sample made with 4 parts of nitric acid to 3 of muriatic acid, had the spec. grav. 2·443, and had 4 equivs. of tin to 1 of acid.

These highly basic combinations keep well except in the hottest summer weather. They unite with water in all proportions without change. Weak acids produce no alteration of the colour. The alkaline carbonates in excess precipitate a yellow oxide of tin, leaving the liquid colourless. Such nitromuriates show no tendency to crystallize, but by spontaneous evaporation dry down to a tough, shiny, translucent mass, which readily dissolves again in water. In fact, they very much resemble the basic nitrates of iron mentioned in a former volume of this Journal*. And in making the tin solutions, as in adding iron to nitric acid, the reddish colour begins to appear when the compound begins to become basic. Reagents show that the tin exists in neither the highest nor the lowest degree of oxidation. The protochloride of tin cannot be made in the slightest degree basic without precipitation; and the same seems to be true of all protosalts. To be sure, strong chloride of zinc, as we often see in making large quantities, on being tested with metallic zinc, oxidizes and dissolves an excess of the metal, and the solution remains perfect after cooling, but dilution causes an immediate precipitation of oxychloride. The basic nitrates and acetates of lead are, on the other hand, but slightly soluble in cold water; while the basic sesquisalts are uncrystallizable and miscible with water in all proportions.

It was therefore natural to suppose that in the tin-salts in question the tin must be in the form of sesquioxide; and further, that the production of such combinations would settle a hitherto mooted point, by showing that there is a salifiable sesquioxide of tin as truly as a sesquioxide of iron.

And now, to determine whether any fallacious appearances could originate from the nitric acid or the ammonia present, another mode of formation was resorted to. 12 equivs. of protochloride of tin,—

* Chem. Gaz. vol. viii. p. 61.

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the "tin crystals" of commerce,—were dissolved in their own weight of warm water, and one equivalent of crystallized chlorate of potash was added by degrees, as fast as the violent reaction would allow. The result was a clear, high-coloured liquid containing, of course, no foreign matter except a very little chloride of potassium. By adding a solution of nitrate of lead, a red nitrate of tin was formed. Carbonate of lead added to such a nitrate or to the muriate, removed nearly half the acid without any precipitation of tin.

In this way, then, permanent solutions may be made containing about 3 equivs. of tin for 2 of acid, but for some reason they cannot be made more basic without gelatinizing; perhaps because of the great degree of dilution necessary to enable the neutralization of the acid to go on, for it appeared in the direct way of making that a mixture of weaker acids would dissolve much less tin.

But the chlorate of potash process proved too much, since it was found that when 1 equiv. of the chlorate acted on 6 equivs. of the protochloride, the tin was completely oxidized, making a clear and almost colourless liquid. So the permuriate of tin may be basic and yet soluble. And it further appeared on adding carbonate of baryta or carbonate of lead, that two-thirds of the acid might be abstracted without gelatinization. 3 equivs. of bibasic permuriate would bear the addition of 2 equivs. of alkali, and if 3 equivs. of protochloride of tin were also present, it would bear no more, and therefore the basic sesquinitrate might be looked upon as a mixture of protonitrate and basic pernitrate.

Various other experiments have established the hitherto unnoticed fact, that *the soluble salts of binoxide of tin may be made highly basic and yet remain soluble**, a fact of some practical importance, and one which seems likely, in connexion with others already observed, to lead to the more comprehensive generalization, that the soluble salts of the peroxides remain soluble, when the larger part of the acid is abstracted.

As for the existence of true salts of the sesquioxide of tin, there appears to be as yet no other evidence but such as may be drawn from colour. The fact that the sesquioxide dissolved in ammonia, while the protoxide does not, of itself proves nothing, for why might not stannic acid render protoxide of tin soluble in ammonia, just as arsenic acid does the sesquioxide of iron? But the hydrated protoxide and peroxide of tin and their ordinary salts, as well as the stannates, are colourless, while intermediate substances may be formed that are coloured. This becomes strikingly apparent if we make a basic permuriate of tin by oxidizing neutral protochloride

* Gmelin, misled by theoretical reasoning, says, "If a normal stannous salt is to be converted into a normal stannic salt by the action of air or nitric acid, it must first be mixed with a quantity of acid equal to that which it already contains; in default of the requisite quantity of acid, a precipitate is formed during the oxidation, consisting either of the hydrated stannic oxide or a basic salt."—*Handbook*, Cav. Soc's. Ed., v. p. 75.

Now as far as oxidation by nitric acid is concerned, this statement has been found at variance with actual results.

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of tin with chlorate of potash or nitric acid, and then drop into the colourless or slightly yellow solution a few crystals of protochloride of tin, which will presently strike a red colour. This red solution gives a reddish precipitate with alkaline carbonates, thus showing that Fuchs's sesquioxide of tin may not be coloured by iron, as is generally supposed. A mixture of two colourless oxides could not be yellow, and it would be strange if a stannate of a white protoxide were not white. Fremy's metastannate of protoxide of tin, made by digesting metastannic acid in neutral protochloride, is indeed yellow; but is it certain that SnO, $Sn^5 O^{10}$ represents the true composition? At any rate, I find that this product gives with weak hydrochloric acid a greenish-brown solution which darkens somewhat on exposure to sunlight,—a singular action for a true salt composed of colourless constituents.

A brown hue is sometimes developed on dissolving in hot water the residue obtained by boiling tin in strong sulphuric acid. Again, crystallized protochloride of tin, when kept for a long time in loosely stoppered bottles, is apt to turn yellow, especially on the side next the light.

Colour appears to arise then during the deoxidation of peroxide or of basic persalts, or the oxidation of the protosalts. So unless it can be shown that the olive and the red forms of the protoxide may enter into combination retaining their respective colours, we seem forced to admit the existence of one or more intermediate oxides of tin.—Silliman's *American Journal* 1857, p. 220.

On Gallactic and Pectolactic Acids.
By C. Boedeker *and* C. Struckmann.

200 grms. of sugar of milk and 1000 grms. of pure sulphate of copper are dissolved in hot water, and solution of caustic soda is added to the solution until the precipitate which is produced at first is again dissolved; the whole is then boiled until the peroxide of copper which is reduced by this means has separated as protoxide, 200 grms. of sulphate of copper are added, and it is again boiled; after the protoxide of copper has been separated by filtration, a yellow fluid is obtained. The soda is neutralized by sulphuric acid; the sulphate of soda is allowed to separate by crystallization as far as possible; and the residue is mixed with quartz sand and evaporated to dryness. The brown dry residue is extracted with alcohol, which only takes up chloride of sodium, with some sulphate and pectolactate of soda (but no formiate of soda).

The residue from the treatment with alcohol is dissolved in water, and the solution is precipitated with acetate of baryta. A small quantity of humoid matter, produced by the decomposition of the sugar, is then precipitated by a few drops of acetate of lead until the lead precipitate becomes white; it is then filtered and completely precipitated by acetate of lead. The washed lead precipitate is decomposed by sulphuretted hydrogen, and the filtrate evaporated to a syrup. This is dissolved in alcohol, filtered if necessary, and

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the solution, after being diluted with water, is precipitated again with acetate of lead. This precipitate is again decomposed by sulphuretted hydrogen. The solution filtered from the sulphuret of lead is then nearly colourless, and when evaporated on the water-bath furnishes

Gallactic Acid, a bibasic acid, the salts of which are represented by $2RO + C^{14} H^3 O^7$. The pure acid, when concentrated as much as possible, forms an uncrystallizable, clear, tenacious, syrupous, yellow fluid; it is inodorous, and only has a slight fruit-like odour when heated; it tastes, something like malic acid, very sour. When heated upon platinum-foil it becomes strongly inflated and melts, smells like malic acid, then inflames, and at last the light shining coal burns away completely. It cannot be volatilized without decomposition. It may be mixed both with water and alcohol in any proportion; in æther it is insoluble.

Its aqueous solution is not rendered turbid by lime-water, as long as the mixture remains acid; as soon as it becomes alkaline, a lime-salt is thrown down. Chloride of calcium, baryta-water (even added in excess), chloride of barium, protochloride of zinc, sulphate of copper, bichloride of mercury, perchloride of iron, and nitrate of silver produce no turbidity. Protonitrate of mercury, like the pernitrate, furnishes a white, flocculent precipitate. Acetate of iron gives a strong reddish-brown precipitate. When boiled with Fehling's solution and caustic soda, it produces no reduction of protoxide of copper. Both neutral and basic acetate of lead precipitate a pulverulent, white lead-salt.

The salts formed by gallactic acid with potash, soda, ammonia, and baryta are extremely soluble in pure water, and partly deliquescent; both the neutral and acid salts are uncrystallizable, and after the evaporation of the aqueous solutions, both in the cold and by heat, they remain as amber-yellow, transparent, very hygroscopic masses. When their aqueous solutions are not too much diluted, they are thrown down in the form of a pure white flocculent precipitate by a sufficient quantity of alcohol, but on standing, the white flakes coalesce rapidly and form a yellow, varnish-like coating upon the walls of the glass.

Gallactate of Lime, $2CaO + C^{14} H^3 O^7 + 3HO$.—When the acid is saturated with marble or milk of lime, a sticky, varnish-like substance is obtained by evaporation. But if a little excess of lime-water be added, a flocculent white precipitate is formed, which may be easily washed with weak alcohol. Dried over sulphuric acid at the ordinary temperature, its analysis gave—

CaO	24·52	24·48	2 = 56	24·78
$C^{14} H^3 O^7$	..	..	1 153	63·27
HO	13·28	..	3 27	11·95

Dried at 212° F. the salt $2CaO + C^{14} H^3 O^7$ was found to contain 28·28 and 28·24 per cent. of lime (calculated 28·14).

Gallactate of Magnesia and *Gallactate of Zinc* are very soluble in water, and completely non-crystalline; they dry into varnish-like

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masses. They are precipitated by alcohol from the aqueous solution in white flakes.

Gallactate of Iron is precipitated in reddish-brown flakes by acetate of iron.

Gallactate of Copper is thrown down as a slimy, pale blue precipitate, when persalts of copper are mixed with a neutral alkaline gallactate, but not with the free acid.

Gallactate of Lead, $2PbO, C^{14} H^3 O^7 + 6HO$, is precipitated from neutral acetate of lead on the addition of free gallactic acid in the form of a heavy pulverulent precipitate. When dried over sulphuric acid at the ordinary temperature, it gave on analysis,—

PbO	53·96	2	=223·4	53·14
C	19·83	14	84·0	19·98
H	2·11	9	9·0	2·14
O	24·10	13	104·0	24·74

When dried at 248° F. its composition is $2PbO, C^{14} H^3 O^7 + 3HO$.

Protogallactate of Mercury forms a heavy white powder, which is insoluble in water, and soluble with difficulty in dilute nitric acid. It is precipitated by free gallactic acid from protonitrate of mercury.

Pergallactate of Mercury, $2HgO, C^{14} H^3 O^7 + 3HO$.—With a solution of the free acid pernitrate of mercury gives a white, amorphous precipitate, which is pale yellow when dried. Dried over sulphuric acid, its composition is—

HgO	55·03	2	=216	55·96
$C^{14} H^3 O^7$	37·05	1	143	37·04
HO	7·92	3	27	7·00

When dried at 248° F. it is $2HgO, C^{14} H^3 O^7$.

If instead of an excess of peroxide of copper a smaller quantity than is necessary for the oxidation of the sugar of milk be employed, pectolactic acid is formed. It is not precipitated by neutral acetate of lead, and consequently remains in solution during the preparation of gallactic acid. From this it is precipitated by basic acetate of lead, and it is prepared from the lead precipitate in the same way as gallactic acid.

Pectolactic Acid, $C^{16} H^6 O^{10} + 2HO$, is exactly similar to gallactic acid; it is uncrystallizable, syrupous, brownish-yellow, and deliquescent in the air when it has been dried into a varnish-like mass at a high temperature; it has a harsh, acid taste, and no perceptible odour; when heated it behaves like gallactic acid. It is soluble in water and alcohol in all proportions, but insoluble in æther.

With both lime-water and baryta-water it may be mixed in any proportion without producing a precipitate; the acid neutralized with lime-water is not precipitated even by alcohol, but if baryta-water be employed to neutralize it, a white, flocculent precipitate is thrown down by alcohol; this coalesces and coats the surface of the glass with a transparent sticky varnish.

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Chlorides of calcium, barium, iron, and mercury, protosulphate of iron, sulphate of copper, protonitrate of cobalt, nitrate of silver, sulphate of alumina and potash, and acetate of lead do not precipitate the free acid. Acetate of iron gives a reddish-brown, flocculent precipitate with the free acid. Protonitrate of mercury gives a white, flocculent precipitate, as does the pernitrate, but this is soluble in an excess of the precipitant. When boiled with Fehling's solution of copper no change is produced in dilute solutions by the first boiling, but if the whole be then left standing only for a short time, yellowish-red flakes often separate suddenly; with more concentrated solutions a strong reduction of protoxide of copper takes place immediately. With nitrate of silver, the acid exhibits no alteration in the cold; if they be boiled together, the fluid becomes of an intense yellow colour, as when sugar is boiled with caustic potash; if a very small quantity of ammonia be then added, the fluid becomes brownish-purple, and on boiling it, the wall of the glass is covered with a silver speculum, more beautiful than that obtained with sugar of milk, aldehyde, &c.

When this acid is previously neutralized by an alkali, perchloride of iron produces a strong, yellow, flocculent precipitate, which dissolves readily in caustic soda. Neutral acetate of lead gives a copious, white, flocculent precipitate, which dissolves again in an excess of the reagent. Sulphate of copper produces a pale blue, gelatinous precipitate, which is readily soluble in caustic soda. Nitrate of silver gives a white, flocculent precipitate. Nitrate of cobalt, a reddish flocculent precipitate. Acetate of iron, when slowly and cautiously added, gives no precipitate at first, because the iron salt is soluble in the excess of the alkaline pectolactate; if more be added gradually, a strong, flocculent, reddish-brown precipitate is produced, often suddenly.

The acid dried over sulphuric acid still retains 5 equivs of water; it is $2HO + C^{16} H^6 O^{10} + 5HO$. The analysis of this acid is given under A, and that of acid dried at 212° F. under B:—

	A.			B.			
C	39·10	16 =	19	39·18	43·48	16 = 96	44·04
H	6·10	13	13	5·31	5·48	10 10	4·59
O	54·80	17	136	55·51	51·04	14 112	51·37

Pectolactate of Baryta, $2BaO, C^{16} H^6 O^{10} + 9HO$, is readily soluble in water, insoluble in alcohol, and non-crystalline, and forms amber-yellow crusts, which become sticky and tough when exposed to the air. When triturated with absolute alcohol it forms a white powder.

Pectolactate of Zinc is a white, flocculent precipitate, insoluble in water, readily soluble in an excess of acid.

Pectolactate of Cobalt is a lilac-coloured, flocculent precipitate, with the same solubility as the preceding.

Pectolactate of Copper is light greenish-blue; solubility as in the the preceding. It is also soluble in caustic soda.

Pectolactate of Silver, a white, flocculent precipitate, soon becoming brown, and readily soluble in excess of acid.

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Protopectolactate and *Perpectolactate of Mercury* form heavy white flakes, which are insoluble in free pectolactic acid, and rather difficult of solution, even in dilute nitric acid.

Pectolactate of Lead.—The neutral salt is soluble both in an excess of free acid and in acetate of lead, but not in water; the basic salt is insoluble in acetate of lead, but otherwise resembles the neutral salt. Both form heavy, white, pulverulent precipitates.

Pectolactate of Iron.—By precipitating a neutral solution of pectolactate of ammonia with acetate of iron, a rust-coloured precipitate of basic pectolactate of iron is obtained; this is insoluble in free acid, but soluble in caustic soda.

When dried over sulphuric acid this salt has the composition $6Fe^2O^3+C^{16}H^6O^{10}+14HO$. When dried at 212° F. it is $6Fe^2O^3+C^{16}H^6O^{10}+8HO$. At 248° F. it is $6Fe^2O^3+C^{16}H^6O^{10}$. This acid is therefore also bibasic $=2HO+C^{16}H^6O^{10}$.

In the formation of gallactic acid from sugar of milk no carbonic acid is evolved from the latter. Water and gallactic acid are the only products of oxidation when an excess of oxide of copper is employed. As regards quantities, not quite 7 equivs. of CuO are reduced by 1 equiv. of sugar of milk, $C^{12}H^{12}O^{12}$.—Liebig's *Annalen*, c. p. 264.

On Chlorobenzoic Acid. *By* H. Limpricht *and* L. von Uslar.

In the distillation of protochloride of sulphobenzoyle, protochloride of chlorobenzoyle passes over. The decomposition appears to take place according to the equation

$$C^{14}H^4S^2Cl^2O^6=C^{14}H^4Cl^2O^2+S^2O^4.$$

At the same time, however, much carbon separates, probably as a secondary product. The distillate is converted by boiling with water into muriatic acid and chlorobenzoic acid, $C^{14}H^5ClO^4$. It is most easily obtained from the protochloride by boiling with potash, and precipitation by muriatic acid. It forms small yellow needles, which are obtained perfectly white by repeated combination with a base, and separation therefrom by means of an acid.

The acid dissolves with difficulty in cold, but easily in hot water; it is soluble in alcohol and æther; from the alcoholic solution it crystallizes in small prisms united concentrically; the crystals never resemble those of salicylic acid. It fuses at about 284° F., but sublimes even below this in small needles. Analysis:—

C	52·9	14	53·5
H	3·3	5	3·2
Cl	..	1	22·9
O	..	4	20·4

The solution of the ammoniacal salt loses much ammonia during evaporation, and leaves behind nearly pure chlorobenzoic acid. The potash and soda salts could not be obtained crystallized.

Chlorobenzoate of Baryta, $C^{14}H^4BaClO^4+3HO$.—Small acicular

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crystals, readily soluble in water, which lose their water of crystallization at 212° F.

				Calculated.
Water	10·2	..	..	10·8
Barium	..	30·3	30·2	30·4

Chlorobenzoate of Lime, $C^{14} H^4 CaClO^4 + 3HO$.—Small, scaly, readily soluble crystals; they lose their water of crystallization at 212° F.

	Found.	Calculated.
Water	13·2	13·3
Calcium.....	11·5	11·3

The lead-salt is a white precipitate, which, after being dried over sulphuric acid, loses nothing more in weight at 230° F., but becomes partially fused and yellow.

The copper-salt is a green precipitate.

Chlorobenzoate of Silver, $C^{14} H^4 AgClO^4$.—A white precipitate consisting of microscopic needles.

Silver 41·2 per cent. found, 40·9 per cent. calculated.

Nitrochlorobenzoic Acid, $C^{14} H^4 (NO^4) ClO^4$. — Chlorobenzoic acid dissolves slowly in fuming nitric acid; if after a few hours the solution be mixed with water, no precipitate is produced at once, but in the course of several days limpid prisms of nitrochlorobenzoic acid are deposited. They are readily soluble in alcohol and æther, and crystallize in prisms on the spontaneous evaporation of the ætherial solution; in water they melt when heated, and dissolve at a boiling heat, but do not separate again on cooling. The dry acid only fuses at 244°·4 F.

Nitrochlorobenzoate of Baryta, $C^{14} H^3 Ba (NO^4) ClO^4 + 2HO$.—Readily soluble, warty crystals, which lose their water of crystallization at 212° F.

	Found.	Calculated.
Water	6·4	6·3
Barium.....	25·6	25·4

Nitrochlorobenzoate of Silver, $C^{14} H^3 Ag (NO^4) ClO^4 + HO$ (?).—Nitrate of silver throws down small, shining laminæ from the concentrated solution of the acid; these do not become black when the solution is boiled, and are tolerably soluble in water.

Silver, calculated according to the formula $C^{14} H^3 Ag (NO^4) ClO^4 + HO$ = 34·0 per cent., found 33·8 per cent.

Chlorobenzoic Æther, $C^{14} H^4 Cl (C^4 H^5) O^4$.—The protochloride is heated with alcohol, or the acid with alcohol and sulphuric acid. It forms a fluid smelling like benzoic æther, and boiling at about 473° F. Chlorine, found 19·0 per cent; calculated 19·1 per cent.

It dissolves in a mixture of 2 parts of English sulphuric acid and 1 part of concentrated nitric acid; if this solution be diluted after 24 hours with water, an oil separates, which becomes converted into crystals in the course of a short time. These are undoubtedly nitro-

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chlorobenzoic æther; they may be obtained limpid and of large size from an alcoholic solution.

Protochloride of Chlorobenzoyle, $\left.\begin{matrix} C^{14} H^4 ClO^2 \\ Cl \end{matrix}\right\}$. As already observed, this compound occurs as a product of decomposition of protochloride of sulphobenzoyle. It is the best plan to heat 1 equiv. of sulphobenzoic acid and 2 equivs. of perchloride of phosphorus in a retort as long as fluid products of distillation pass over, and to rectify these with an immersed thermometer. By repeated rectifications a yellowish liquid boiling at about 545° F. is obtained, which is decomposed in a few hours by boiling water into muriatic and chlorobenzoic acids, and is also slowly attacked by dilute potash and ammonia; with concentrated aqueous ammonia, on the other hand, it immediately forms chlorobenzamide and muriate of ammonia. These decompositions indicate the protochloride of chlorobenzoic acid. In the analysis, however, it appeared that it was still contaminated with other substances which could not be removed by distillation, as too little chlorine (34·3 and 34·9 per cent.) was found, and there was still some sulphur (1·0 per cent.).

The protochloride prepared from chlorobenzoic acid with perchloride of phosphorus, on the contrary, was a limpid, strongly refractive fluid, boiling at about 437° F.

Chlorine, found 40·4 per cent., calculated 40·6 per cent.

Chorobenzamide, $N \left\{\begin{matrix} C^{14} H^4 ClO^2 \\ H \\ H \end{matrix}\right.$. Laminar crystals, obtained by the solution of protochloride of chlorobenzoyle and concentrated ammonia; readily soluble in alcohol and hot water, sparingly so in cold water; fusible at 251°·6 F. Analyses:—

C	54·8	54·3	..	14	53·8
H	4·5	4·3	..	6	3·9
Cl	..	..	..	1	23·0
N	..	..	8·7	1	9·0
O	..	..	..	2	10·3

According to Chiozza, the chlorobenzoic acid prepared by him by the distillation of salicylic acid with perchloride of phosphorus and decomposing the distillate with water, has a great resemblance to salicylic acid. According to the authors this is not identical with the acid prepared by them.

Chlorobenzoic acid from salicylic acid fuses at about 266° F., the baryta-salt contains no water of crystallization, the lime-salt 2 equivs. Analysis gave,—

	Found.	Calculated according to $C^{14} H^4 CaClO^4 + 2HO$.
Water..	9·3	9·3
Calcium	11·2	11·3

Chlorobenzoic acid from sulphobenzoic acid fuses at about 284° F., the baryta-salt contains 3 equivs. of water of crystallization, as does also the lime-salt.—Liebig's *Annalen*, cii. p. 259.

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ANALYTICAL CHEMISTRY.

Determination of Peroxide of Iron and Alumina. *By* Dr. GRÄGER.

AFTER alumina and oxide of iron have been precipitated by ammonia and washed in the usual manner, the precipitate is dissolved in the smallest possible quantity of muriatic acid, the fluid is neutralized with ammonia, when even a slight precipitation is not injurious, the oxide of iron and alumina are then thrown down by sulphuret of ammonium, the precipitate produced is immediately dissolved again in a slight excess of muriatic acid, and the sulphuretted hydrogen is removed by gently heating it in a beaker. It is not necessary to filter the fluid, even when it is rendered considerably turbid by separated sulphur; it is then tested with bichromate of potash, and the quantity of oxide of iron is thus found. It is now filtered, and the whole is precipitated with ammonia, the precipitate is washed on the filter, dried, calcined, and weighed. Its weight, minus that of the oxide of iron found, and that of the oxide of chrome produced, is that of the alumina.

If the substance to be investigated contain protoxide of iron besides alumina and peroxide of iron, and it is desired to determine the quantity of this separately, the process is somewhat changed. In this case washed sulphuretted hydrogen is conducted through the perfectly clear fluid, free from nitric acid and chlorine, until all the oxide of iron is converted into protoxide; the separated sulphur is then collected on a filter, dried, and weighed. Its weight is referred to the oxygen of the oxide of iron. The further process is the same as above described, *i. e.* the fluid is tested with bichromate of potash, and then precipitated by ammonia; the oxides of iron and chrome are deducted from the weight of the precipitate, when the alumina constitutes the residue. From the weight of the oxide of iron the weight first found by sulphuretted hydrogen is deducted, and the rest of the oxide of iron is converted by calculation into protoxide of iron. Of course, even in the first case, when all the iron is present as peroxide, its reduction may be effected by sulphuretted hydrogen; but by this means nothing is gained, for instead of testing with bichromate of potash, the protoxide of iron must be oxidized by chlorine or nitric acid, in order to allow the oxide of iron to be precipitated by ammonia together with the alumina. When, in the second case, the quantity of oxide of iron present, as shown by the sulphur separated, is very small, it is better to convert the latter, with the filter, into sulphuric acid by nitric acid, to precipitate this by a baryta-salt, and calculate the oxygen from the sulphate of baryta.—*Archiv der Pharm.*, cxl. p. 300.

On the Behaviour of the Native Metallic Sulphurets towards Muriatic Acid under the influence of Galvanism. *By* M. VON KOBELL.

When copper pyrites is moistened with muriatic acid (1 vol. of concentrated acid to 1 vol. of water), no change takes place in the pyrites; but when the moistened place is touched with zinc, sulphuretted hydrogen gas is evolved, and the pyrites acquires a

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brownish colour. When iron is employed in place of zinc, no action appears to take place; nevertheless this is remarkably shown when fine powder of copper pyrites is mixed with fine powder of iron and treated with muriatic acid. Sulphuretted hydrogen gas is evolved in abundance; and if 2 parts of iron be taken to 1 part of pyrites, the latter is easily decomposed without the aid of heat, and the copper is precipitated, whilst in the absence of iron it is but slowly attacked by muriatic acid even when boiled.

Other sulphurets behave in the same way as copper pyrites, and this comportment may therefore be made use of in ascertaining the presence of sulphur in them. For this purpose the author employs a cylindrical glass, about 2½ inches in height and 1 inch in diameter, puts into it equal volumes of the specimen and iron powder (of each as much as can be taken up on the point of a knife), and pours over the mixture dilute muriatic acid to a depth of some lines. He then closes the glass with a suitable cork, which holds a strip of paper soaked in acetate of lead and then dried, in such a way that it passes across the whole width of the cork, and projects on each side when the glass is closed. With the following minerals the reaction for sulphur makes its appearance within one minute, the paper becoming yellow, brownish, or gray.

Antimonite.
Pyrostibite.
Argentite.
Stephanite.
Proustite.
Pyrargyrite.
Polybasite.
Aftonite.
Chalkosine.
Covelline.
Tetraedrite.
Tennantite.
Polytelite.
Spaniolite.
Chalcopyrite.
Bornite.
Stannine.
Bismuthine.
Galenite.
Geokronite.
Bournonite, colour of paper pale yellow.
Boulangerite.
Plumosite.
Dufrenoysite.
Jamesonite.
Plagionite.
Zinkenite.
Kobellite.
Saynite.
Gersdorffite (as also amoibite).
Cobaltine, colour pale yellow.
Pyrites, marcasite, lonchidite, kyrosite.
Arsenopyrites.
Hauerite.
Sphalerite.
Cinnabar.
Linneite.
Nagyagite.
Tetradymite, colour pale yellow.

All these compounds, and of course also pyrrhotine (and sulphuret of iron and nickel), alabandine and Berthierite, which evolve sulphuretted hydrogen, even by themselves, when treated with muriatic acid, show the above-mentioned coloration of the lead-paper within one minute. On the other hand, realgar, orpiment, and molybdenite give no reaction. Sulphur itself, however, reacts in the way above mentioned. By this means very similar minerals may be distinguished at once, for example, Clausthalite and Galenite, for seleniuret of lead gives no reaction, chloanthite and arsenopyrites, &c.

Iron powder is a carburet of iron (known in the shops as *Ferrum alcoholisatum*); of course it must be free from sulphur when employed in these experiments.—*Gelehrte Anzeigen der königl. bayer. Akad. der Wiss.*, and *Journ. für Prakt. Chemie*, lxxi. p. 146.

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On Molybdate of Ammonia as a Reagent for Silicic Acid.
By W. KNOP.

If a splinter of rock-crystal be fused with pure potash in order to obtain a specimen of pure water-glass, and the fused mass be dissolved in water and supersaturated with muriatic acid, this clear solution gives the same reactions with molybdate of ammnoia as fluids which contain traces of phosphoric acid. If it be dropped into the fluid which is obtained by dissolving molybdate of ammonia in water and adding nitric acid until it becomes clear, the latter becomes citron-yellow. If it contains much molybdate and little muriate of ammonia, a nearly white precipitate settles in the course of a few hours or days, and the fluid remains yellow. If the fluid contains much muriate of ammonia, a strong citron-yellow precipitate is thrown down in a couple of hours.

Our best text-books have adopted molybdate of ammonia as a reagent for phosphoric acid, at a time when few observations had yet been made upon it. Thus in Rose's 'Handbuch der Analyt. Chemie,' 1851, p. 526, we read, "No other acid, except arsenic acid, behaves with molybdate of ammonia similarly to phosphoric acid."

This statement is to be corrected, as we see that the acids which are unalterable by fire also behave pretty similarly towards molybdate of ammonia. (Boracic acid does not colour molybdate of ammonia.)

The reaction (the yellow coloration) which dissolved silicic acid produces in the solution of molybdate of ammonia in nitric acid, is as distinct as any other. The addition of free ammonia causes the yellow colour to disappear; it reappears after fresh supersaturation with nitric acid.

From this behaviour it appears unmistakeably that many of the statements hitherto made with regard to the occurrence of phosphoric acid are erroneous; wherever, in testing minerals for phosphoric acid, the silica was not completely got rid of previously, it has been taken for phosphoric acid. Acetate of uranium is not thrown down by free silica. But if phosphoric acid and silica be present together in the same fluid, the precipitate of phosphate of uranium may contain silica.—*Chemisches Centralblatt*, Sept. 30, 1857, p. 691.

On a simple Method of determining the Carbon in Cast Iron.
By Professor VON KOBELL.

When finely triturated pyrolusite or manganite is brought in contact with iron-powder and muriatic acid (1 vol. concentrated acid and 1 vol. water), an energetic action takes place. Whilst the finely-pounded ores of manganese by themselves are only dissolved very slowly without the aid of heat, they dissolve with ease when mixed with iron. 2 grms. of pyrolusite, with 1 grm. of iron, and 1½ cub. inch of muriatic acid, dissolved completely within two minutes when well shaken. At the same time the temperature of the fluid rose

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from 59° to 133° F., and only a very small evolution of gas was perceptible, as the chlorine evolved by the pyrolusite and the carburetted hydrogen gas simultaneously evolved by the iron decompose one another, and the carbon is separated.

This behaviour may be applied to the determination of the amount of carbon contained in cast iron, &c. For 3·5 parts of iron (1 equiv.), 5·44 parts of pyrolusite (1 equiv.) are to be taken. In order to obtain perfect contact, however, it is advisable to take rather more of the latter, about 1 part of iron and 2 parts of pyrolusite, as in the above experiment, and to add the iron by degrees to the acid with constant agitation, or the muriatic acid in the same way to the mixture. Manganite and Crednerite, $(CaO, MnO)^3 + 2Mn^2O^3$, behave in a similar manner.—*Gelehrte Anzeigen der königl. bayer. Akad. der Wiss.*

Basic Nitrate of Bismuth as a reagent for Grape-Sugar.
By Professor Böttger.

In testing urine for example, for sugar, if 1 volume of urine be boiled with an equal volume of a solution of 1 part of crystallized carbonate of soda in 3 parts of water, and a very small quantity of basic nitrate of bismuth be added to it, the latter becomes gray by reduction, if grape-sugar be present. Cane-sugar does not possess this property, and none of the other bodies occurring in the urine blacken the bismuth salt.—*Journ. für Prakt. Chemie*, lxxi. p. 431.

On some Characteristics of Tellurium Ores.
By Professor von Kobell.

The well-known blowpipe test by which a tellurium ore in an open glass tube gives a sublimate, which fuses into colourless drops of oxide of tellurium when the tube is heated at the situation occupied by the deposit, is not always sufficiently distinct, and the characteristic drops are frequently hardly distinguishable with the lens. The author has therefore endeavoured to employ the behaviour of tellurium to sulphuric acid as a character. The powdered ore is placed in a glass tube closed at one end, of 4 to 5 lines in diameter and about 6 inches long; concentrated sulphuric acid is poured over it to a depth of 1 inch, and it is heated over the spirit-lamp. Immediately upon the first application of heat, the acid acquires a fine red colour with pure tellurium, sylvanite, and tetradymite, but when the heat is increased, the colour again disappears. If water be added to the red fluid, a blackish-gray precipitate of tellurium is formed and the fluid becomes colourless.

Nagyagite behaves differently; by heating with concentrated sulphuric acid, a turbid brownish fluid is obtained, which exhibits a hyacinthine colour when it has been left standing for some time. With water, it gives a similar precipitate to the preceding, and also loses its colour. In this way the ores of tellurium are easily recognizable; the ores of selenium, treated in the same way, do not colour sulphuric acid.—*Gelehrte Anzeigen der königl. bayer. Akad. der Wiss.*

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THE CHEMICAL GAZETTE.

No. CCCLXIII.—December 1, 1857.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Compounds of Tartaric Acid with Saccharine Matters. By M. BERTHELOT.

In continuing the investigation of the compounds formed by saccharine matters I have been led to produce with mannite, dulcine, and glucose, acid compounds of a very peculiar nature. These compounds are distinguished by their acid character from the neutral compounds which I have already described, but they present the same general relations between their constituent elements. They establish the passage between the vinic acids formed by the ordinary alcohols, and a great number of natural compounds analogous to tannine, and capable of being split up with fixation of water, and simultaneous formation of glucose and a corresponding acid.

In the present memoir, I shall confine myself to indicating the compounds produced by the union of tartaric acid with glucose, sugar of milk, cane-sugar, sorbine, pinite, quercite, and erythroglucine; I have already described an analogous compound formed by mannite and tartaric acid, and I shall indicate the existence of a compound of glucose and citric acid.

All these bodies are prepared and purified by the following process:—equal weights of tartaric acid and saccharine matter are intimately mixed, and the whole is heated to 248° F. for a day or two in an open vessel. This done, the cooled mass is triturated with a little water and carbonate of lime. When the saturation is completed, the excess of carbonate of lime and the regenerated tartrate of lime are separated by filtration.

The liquid contains the lime-salt of the complex acid, mixed with the uncombined excess of saccharine matter; the solution is precipitated by adding to it twice its volume of alcohol; the mother-liquor is decanted, and the precipitate collected on a filter and washed with alcohol, diluted with its volume of water. This second series of operations separates the lime-salt from the excess of saccharine matter.

The lime-salt is redissolved in water and precipitated again with alcohol; this double manipulation is repeated a third time, and in this way the last traces of tartrate of lime and of saccharine matter are separated, and the lime-salt of the complex acid is obtained in

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an isolated state. This is dried *in vacuo*, or at 230° F., and analysed.

It is sufficient to dissolve this salt in water, and treat it with a calculated proportion of oxalic acid, to obtain the complex acid.

The following are the combinations which I have prepared and analysed:—The formulæ which I propose express the most simple relations which are capable of representing the numbers furnished by analysis; they show that the saccharine body, diminished by a certain quantity of water, like the alcohol in the sulphovinates, replaces in the presence of the acid a portion of the base necessary to saturate this acid in the isolated state. These formulæ, besides, enter for the most part into the same general types as the neutral compounds formed between acids and glycerine. From this latter analogy, it is probable that, according to circumstances, one and the same saccharine matter may form several acid compounds with tartaric acid; I shall only signalize those which I have obtained.

1. *Dulcitartaric Acid*, formed by the union of dulcine with tartaric acid in equal equivs.; monobasic. Analogous to the glyceritartaric acid of Berzelius:—

$$C^{14}\,H^{10}\,O^{15} = C^{6}\,H^{6}\,O^{5} + C^{8}\,H^{6}\,O^{12} - 2HO\,*.$$

Dulcitartrate of lime, dried at 230° F.: $C^{14}\,H^{9}\,CaO^{15}, 4HO$.

2. *Pinitartaric Acid*, formed by the union of 1 equiv. of pinite with 3 equivs. of tartaric acid; tribasic. Analogous to mannitartaric acid:—

$$C^{30}\,H^{18}\,O^{35} = C^{6}\,H^{6}\,O^{5} + 3C^{8}\,H^{6}\,O^{12} - 6HO.$$

Pinitartrate of lime: $C^{30}\,H^{15}\,Ca^{3}\,O^{35}, 6HO$.

3. *Quercitartaric Acid*, formed by the union of 1 equiv. of quercite with 2 equivs. of tartaric acid; tribasic:—

$$C^{22}\,H^{16}\,O^{27} = C^{6}\,H^{6}\,O^{5} + 2C^{8}\,H^{6}\,O^{12} - 2HO.$$

Quercitartrate of lime: $C^{22}\,H^{13}\,Ca^{3}\,O^{27}, 2HO$.

4. *Erythroglucitartaric Acid*, formed by the union of 1 equiv. of erythroglucine (containing C^{12}) with 4 equivs. of tartaric acid. Analogous to the preceding by the relations which exist between the carbon of the acid, the carbon of the saccharine body, the lime of the calcareous salt, and the quantities of water eliminated:—

$$C^{44}\,H^{35}\,O^{56} = C^{12}\,H^{15}\,O^{12} + 4C^{8}\,H^{6}\,O^{12} - 4HO,$$

or

$$C^{22}\,H^{17\frac{1}{2}}\,O^{28} = \tfrac{1}{2}(C^{12}\,H^{15}\,O^{12}) + 2C^{8}\,H^{6}\,O^{12} - 2HO.$$

Erythroglucitartrate of lime:—

$$C^{44}\,H^{29}\,Ca^{6}\,O^{56}, 4HO,$$

or

$$C^{22}\,H^{14\frac{1}{2}}\,Ca^{3}\,O^{28}, 2HO.$$

5. *Sorbitartaric Acid*, formed by the union of sorbine and tartaric acid at 212° F.

* These dulcinic compounds must be represented, not by dulcine, $C^{6}\,H^{7}\,O^{6}$, but by dulcinane, $C^{6}\,H^{6}\,O^{5}$, a compound isomeric with mannitane, and formed under analogous circumstances.

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6. *Lactotartaric Acid*, formed by the union of sugar of milk and tartaric acid; bibasic:—

$$C^{34}H^{26}O^{38}=3C^6H^6O^6+2C^8H^6O^{12}-4HO.$$

Lactotartrate of lime, $C^{34}H^{24}Ca^2O^{38}$, 2HO. This salt reduces potassio-tartrate of copper; when treated with nitric acid, it furnishes a large quantity of mucic acid. It is probable that this salt is formed, not by ordinary sugar of milk, but by modified sugar of milk.

In a preparation made under slightly different conditions, the lime-salt obtained corresponded with the formula $C^{22}H^{13}Ca^3O^{28}$, 4HO. It consequently entered into the same type as the quercitartrate of lime.

7. *Cane-sugar* and *Tartaric Acid* (at 212° F.).—This compound is analogous to glyceritartaric and dulcitartaric acids; it contains modified cane-sugar, and reduces potassio-tartrate of copper; monobasic:—

$$C^{14}H^{10}O^{16}=C^6H^6O^6+C^8H^6O^{12}.$$

Lime-salt: $C^{14}H^9CaO^{16}$.

8. *Glucocitric Acid.*—This body is prepared in the same way as the preceding. I have obtained the salts of lime and magnesia.

9. *Salicine* and *Tartaric Acid*.....

10. *Glucotartaric Acid*, formed by the union of 1 equiv. of glucose and 2 equivs. of tartaric acid; bibasic:—

$$C^{22}H^{13}O^{25}=C^6H^5O^5+2C^8H^6O^{12}-4HO.$$

Glucotartrate of lime: $C^{22}H^{11}Ca^2O^{25}$, 2HO. It reduces potassio-tartrate of copper, and does not ferment when in contact with yeast. Treated with dilute sulphuric acid, it is resolved into tartaric acid and fermentescible sugar.

Glucotartrate of magnesia: $C^{22}H^{11}Mg^2O^{25}$, 2MgO, 2HO; crystalline.

Glucotartrate of lead: $C^{22}H^{12}PbO^{25}$. This salt is acid. The neutral salt is insoluble.

From some experiments it appears to me that an acid analogous to, or identical with glucotartaric acid is met with in the grape towards the period of its maturity.

According to the preceding facts, the compounds of tartaric acid with saccharine matters prepared by me belong to four distinct types, of which three are formed under the same conditions as the neutral compounds produced by the union of glycerine with acids.

Thus monacetine ..... $C^4H^4O^4+C^6H^8O^6-2HO$
corresponds with
Glyceritartaric acid ..... $C^8H^6O^{12}+C^6H^8O^6-2HO$
Dulcitartaric acid ..... $C^8H^6O^{12}+C^6H^6O^5-2HO$
and the compound formed by
modified cane-sugar ..... $C^8H^6O^{12}+C^6H^6O^6-2HO$.

Only that the monobasic acetic acid produces a neutral compound with elimination of 2 equivs. of water, whilst the bibasic tartaric

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acid forms acid and monobasic compounds. These compounds are analogous to the sulphovinates.

Diacetine ..... $2C^4H^4O^4+C^6H^8O^6-4HO$

corresponds with

Glucotartaric acid.. $2C^8H^6O^{12}+C^6H^5O^5-4HO$, bibasic,

Quercitartaric acid $2C^8H^6O^{12}+C^6H^6O^5-2HO$, tribasic,

Erythroglucitartaric acid..... $2C^8H^6O^{12}+\frac{1}{2}(C^{12}H^{15}O^{12})-2HO$ } tribasic.

and one of the lactotartaric acids.. $2C^8H^6O^{12}+C^6H^6O^6-2HO$ }

Only that the monobasic acetic acid produces a neutral compound with elimination of 4 equivs. of water, whilst the bibasic tartaric acid forms bibasic or tribasic acid compounds, according to the proportions of water eliminated.

Triacetine ..... $3C^4H^4O^4+C^6H^8O^6-6HO$

corresponds with

Mannitartaric acid .. $3C^8H^6O^{12}+C^6H^6O^5-6HO$

and Pinitartaric acid .... $3C^8H^6O^{12}+C^6H^6O^5-6HO$.

Only that the monobasic acetic acid produces a neutral compound with elimination of 6 equivs. of water, whilst the bibasic tartaric forms acid and tribasic compounds.—*Comptes Rendus*, August 24, 1857, p. 268.

On the Nitro-Acetic Series. By L. Schischkoff *and* A. Rosing.

The bodies belonging to this series have not hitherto been obtained by the direct substitution of the group NO^4 for hydrogen; fulminic acid containing the group of mononitrated acetic acid ready formed, presents the only starting-point for the study of the nitrated bodies derived from acetic acid.

One of the authors has already shown *, that by fixing the elements of water, trinitrated acetonitryle, instead of giving the corresponding ammoniacal salt of trinitro-acetic acid, becomes decomposed into nitroform, ammonia, and carbonic acid:—

$$C^4(NO^4)^3N+2H^2O^2=C^2(NO^4)^3H+NH^3+C^2O^4.$$

In this reaction the carbonic acid enters into an unstable combination with a part of the undecomposed body, and thus forms bodies of a complex nature, which are still to be investigated †.

Trinitrated acetonitryle, when treated with sulphuretted hydrogen, is reduced in a very exceptional manner; instead of the group NO^4 being replaced by NH^2, we have the group NH^4 which replaces the vapour of hyponitric acid, equiv. for equiv.; thus—

$$C^4(NO^4)^3N+4S^2H^2=8S+C^4(NO^4)^2(NH^4)N+4H^2O^2.$$

* See page 448.

† Trinitrated acetonitryle, heated on the water-bath in a sealed tube with water is decomposed with a terrible explosion; under the ordinary pressure at 212° F. a very lively reaction takes place, without much evolution of gas.

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This body is colourless, crystallizes in needles of great brilliancy, is very soluble in water, but less so in alcohol, and nearly insoluble in æther. When rapidly heated it inflames and fuses; at 212° F., it is volatilized in inappreciable quantities, and possesses an extremely acrid odour.

Oxygenated bodies are usually more soluble and less volatile than hydrogenized bodies; here the case is exactly the reverse.

$\underbrace{C^4(NO^4)^3N}_{\text{Trinitrated aceto-nitryle.}}$ } Very volatile at the ordinary temperature; very soluble in alcohol and æther; nearly insoluble in water.

$\underbrace{C^4(NO^4)^2(NH^4)N}_{\text{Ammoniated binitroacetyle.}}$ } Very slightly volatile at 284° F.; nearly insoluble in æther; very slightly soluble in alcohol; very soluble in water.

From its composition and mode of formation this body may be called *binitro-ammoniated acetonitryle*, or, for brevity, *acetic binitrammonyle*. Although *binitrammonyle* be perfectly neutral with reagents, it possesses the properties of an acid, for a part of its hydrogen may be replaced by metals; if its aqueous solution be boiled with oxide of silver, the liquid, on cooling, furnishes a crystallized salt, which is very explosible, slightly soluble in cold water, but more soluble in hot water. This is a silver-salt of the preceding compound.

	I.	II.		Calculated.
C	9·39	9·41	4	9·41
H	1·19	1·18	3	1·17
N	21·35	..	3	21·96
Ag	41·81	42·00	1	42·35
O	..	..	8	25·11

At the first glance it would seem as if binitrammonyle is nothing but a compound of ammonia with binitrated acetonitrile,—

$$C^4(NO^4)^2(NH^4)^2N = C^4(NO^4)^2HN.NH^3,$$

as is the case with nitroform.

Nitroform being an energetic acid combines directly with ammonia. Here the case is quite different. Binitrammonyle is by no means an ammoniacal salt, for it may be boiled with a solution of 1 part of potash in 2 parts of water without evolving ammonia. After this treatment, the liquid on cooling suddenly solidifies, in consequence of the formation of a potash-salt, probably analogous to the silver-salt above mentioned. Binitrammonyle presents the first example of a replacement of hydrogen by the group ammonium, without the product having the properties of an ammoniacal salt. The product here is an acid, and the hydrogen of this acid, or rather of the ammonium, might perhaps be replaced by another equiv. of ammonium. These facts assist in supporting the hypotheses put forward by Gerhardt to represent the cupro-, argento-, and platino-ammoniacal salts.

By the action of more energetic reagents, binitrammonyle undergoes important modifications. Concentrated sulphuric acid decomposes it slowly, the reaction being assisted by heating the mixture from time to time on the water-bath. An oily layer soon floats on

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the surface of the sulphuric acid, which contains combined ammonia. The reaction is accompanied by a slight evolution of gas; the oily stratum, when decanted and placed in a mixture of ice and salt, crystallizes in large and fine prisms; when removed from the freezing mixture, these crystals melt immediately. From its small quantity (2 grms.), this substance could not be purified; the authors therefore analysed the crystals and mother-liquor separately. The mother-liquor, when refrigerated, becomes viscous before crystallizing; this prevented the crystals from being freed from it, so that the two following analyses present marked differences:—

	I.	II.		Calculated.
C	29·73	28·96	10	30·76
H	0·51	0·57	1	0·51
N	..	36·6	5	35·89
O	..	..	8	67·16

The formula $C^{10} N^5 HO^8$ is that which best represents these results. The rational formula may be regarded provisionally as

$$Cy^3 . C^4 (NO^4)^2 H,$$

like the known compound $Cl^3 C^4 H^3$ (bichlorinated hydrochloric æther). If this rational formula should be confirmed hereafter by the metamorphoses of this body, its formation might be explained by the tendency of the cyanides to become tripled. The group $C^4 (NO^4)^2 H$ would be, in this case, triatomic.

Besides an ammoniacal salt, the sulphuric acid contains in solution a body of the same appearance as the preceding. This was obtained by agitating the acid with æther, but as the quantity was insufficient for analysis, its identity with the body analysed cannot be confirmed.

The body $C^{10} N^5 HO^8$ is explosible by heat, insoluble in water, and dissolves with great difficulty in aqueous ammonia; the solution obtained is deep yellow, and on evaporation furnishes a brown matter of a resinous appearance.

A very concentrated aqueous solution of caustic potash acts quite differently upon binitrammonyle; when the mixture is boiled in a matrass, a great evolution of ammonia is perceived, and by degrees a salt crystallizing in prisms and very slightly soluble in caustic potash is deposited; when there is no more evolution of ammonia, the liquid is allowed to cool, and a further quantity of the salt is obtained. It is very slightly soluble in cold, but very soluble in hot water; it behaves in the same way towards alcohol. On cooling it is obtained in the form of bright yellow spangles of great brilliancy, much resembling picric acid; when heated it explodes. It has a neutral reaction. The analysis of this body, heated to 212° F., gave—

	I.	II.	III.		Calculated.
C	12·46	12·11	12·60	20	12·00
H	0·88	0·82	..	7	0·70
N	16·80	17·00	..	12	16·80
K	27·34	27·51	..	7	27·37
O	..	..	..	54	43·13

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This might perhaps be represented by the formula

$$5\,[C^4(NO^4)^2HK] + 2NO^6K + H^2O^2.$$

As there is no doubt from the analyses of the exactness of the empirical formula, this rational formula seems tolerably probable, especially as trinitrated acetonitryle exhibits the same tendency to form double salts. One of the authors has obtained and analysed a salt of the formula

$$C^4N^{10}H^{14}Ag^2O^{14} = C^4(NO^4)^3N(NH^3Ag)^2O^4 + 2NO^6Am.$$

The compound $C^{90}H^7N^{12}K^7O^{54}$ is decomposed with evolution of gas by dilute acids. Concentrated sulphuric acid causes it to explode.—*Comptes Rendus*, August 24, 1857, p. 273.

On the Artificial Production of an Acid belonging to the Fatty Acid Series, containing 34 atoms of Carbon. *By* Professor Heintz.

The author had previously induced Köhler to make experiments in this direction, but these remained incomplete. After many vain attempts to obtain the cyanocetyle, $(C^{32}H^{33}) + (C^2N)$, required for the production of this acid, by the action of cyanide of potassium, cyanide of mercury, and cyanide of silver upon chlorocetyle, cyanocetyle was obtained in abundance, although not pure, by heating the sulphate of the oxide of cetyle and potash to about 392° F. with cyanide of potassium; it was mixed with a solid body, consisting of a mixture of cetylic æther ($C^{32}H^{33}O$) and palmitylic aldehyde ($C^{32}H^{32}O^2$). This could not be perfectly separated from the cyanocetyle. Heintz therefore boiled this impure cyanocetyle for a long time with an alcoholic solution of potash, when a large quantity of ammonia was evolved. The saponaceous residue in the vessel was dissolved in alcohol with the addition of ammonia, the solution was precipitated with chloride of barium, and the precipitate completely washed with boiling æther. The acid separated from the baryta salt, by partial precipitation and recrystallization, furnished a small quantity of a fatty acid fusing at 151°·2 F., which was hardly perfectly pure, but contained more carbon than stearic acid; its composition being probably $C^{38}H^{38}O^4$, and an acid fusing at 139°·8 F., crystallizing, not in needles, but in scales, and of the perfect purity of which Heintz convinced himself. This is margaric acid, as was proved by the analysis of the acid itself, as well as by that of its baryta and silver salts. It is distinguished from the mixed acid which was formerly called margaric acid, not indeed by its melting-point, but by its crystallizing in scales and not in needles, by its not being decomposable by partial precipitation into stearic and palmitic acids, and by the fact that the melting-point of mixtures of this acid with other acids of the fatty series, especially with stearic acid, does not sink so far below its proper melting-point, as was observed to be the case with the mixture formerly denominated margaric acid. Whilst, according to Gottlieb, there is a mixture of the latter with stearic acid which becomes fluid at 133° F., Heintz has never observed a

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lower melting-point than 139° F. in various mixtures of the true margaric acid with stearic acid.—*Bericht der Akad. der Wiss. zu Berlin*, 1857, p. 417.

On Nitroform. *By* L. Schischkoff.

Some time ago the author proved that fulminic acid is a derivative of carbonic acid and nitroacetic acid, namely,

$$N^3 \left\{ \begin{matrix} (C^2 O^2)^2 \\ C^4 H^2 NO^4 \\ H^2. \end{matrix} \right.$$

He also described trinitroacetonitrile, $C^4 (NO^4)^3 N$, and mentioned that by the action of alcohol or water upon this body, a new crystallizable yellow body is produced, the composition of which is $C^2 (NO^4)^3 H, NH^3$.

This body is *trinitromethylammonium* (*trinitrométhylure d'ammonium*). It furnishes an abundance of ammonia with lime. Concentrated sulphuric acid eliminates from it an acid, which immediately reproduces the ammonia-salt with ammonia. This body is

Trinitromethylhydrogen, $C^2 (NO^4)^3 H$ (*trinitrométhylure d'hydrogène*), or nitroform, a body analogous in its constitution to chloroform, which must be derived from marsh-gas, the replaceable hydrogen in the latter being displaced by NO^4, as in other cases by chlorine, iodine, and bromine.

Nitroform is colourless, solid below 59° F., and crystallizes in cubes or very obtuse rhombohedra. It dissolves readily in water, giving it a yellow colour. It is easily inflammable, has an unpleasant odour and a bitter taste. When suddenly heated it explodes violently. It cannot be distilled under the ordinary pressure of the atmosphere; at 212° F. it is decomposed.

The salts of nitroform are crystallizable, of a beautiful yellow colour, and explosive; they decompose readily, with evolution of gas. Anhydrous nitroform may be preserved in a cool place.

When nitroform is prepared by treating the body $C^2 (NO^4)^3 H, NH^3$ with concentrated sulphuric acid, it collects upon the surface in a stratum which becomes solid on cooling. It is easily purified by recrystallization.

If acetonitrile be treated with solution of potash, a yellow, crystallizable salt is obtained, which also furnishes nitroform as soon as it is brought in contact with concentrated sulphuric acid.—*L'Institut*, 1857, No. 1230.

Chemical Investigation of the Human Lymph. *By* Professor Scherer.

The author obtained from Professor Virchow a small quantity of pure lymph from the human subject. It had already formed a slight coagulum of fibrine of a reddish colour at the bottom of the vessel, and above this there was a clear, somewhat yellowish, tenacious fluid, in a slightly alkaline reaction. Fat-drops could only be observed of it in very small quantity.

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The weight of the whole was 13·456 grms. After the greater part of the clear serum had been poured away, the coagulum with the adherent residue of serum was diluted with water, filtered, well washed and dried; it weighed 0·005 grm. =0·371 to 1000 parts of lymph.

Of the serum poured away, 12·848 grms. gave at 230° F. 0·540 grm. of solid residue and 0·094 grm. of ashes, which had a slightly alkaline reaction, evolved no carbonic acid with nitric acid, and presented a considerable quantity of chlorine, and next to this phosphoric and sulphuric acids, potash in considerable proportion, soda, and a little earthy phosphate and iron. The above results give by calculation for 1000 parts of lymph,—

Water	957·60
Solid parts	42·40
Fibrine with lymph corpuscles ..	0·37
Albumen and extractive matter..	34·72
Inorganic matters	7·31

Unfortunately the small quantity of material at command was insufficient for further investigations.

Although in the present case the amount of water and of organic matters (fibrine and albumen) agree pretty well with the statements of Nasse and Geiger, this is not so much the case with the mineral substances, especially as regards the carbonic and phosphoric acids, of which the former was wanting in the ashes, whilst the latter existed in considerable quantity. The comparatively large amount of potash also has not previously been observed.—*Verhandl. der Würzburg. Phys.-med. Gesellsch.*, and *Journ. für Prakt. Chemie*, lxx. p. 413.

On the Special Affinity of Nitrogen for Titanium.

By F. Wöhler *and* H. Sainte-Claire Deville.

Titanium is capable of combining directly with the nitrogen of the air, and for this reason nothing is more difficult than to obtain titanium perfectly free from nitrogen, all the bodies of a coppery red or brassy yellow colour described by chemists as true titanium, being really only nitrurets of titanium. In ordinary cases it is the oxygen of the air which presents the most energetic opposition to most simple bodies remaining in an isolated state; with titanium, on the contrary, it is the nitrogen of the air which prevents it from preserving the metallic state at high temperatures.

An ordinary crucible surrounded with charcoal and strongly heated is inaccessible to the oxygen of the furnace, but the nitrogen easily penetrates into it and combines with the titanium, if it meets with an incandescent mixture of titanic acid and charcoal. The affinity between the two bodies is so great, that if titanium be reduced according to the method of Berzelius by placing fluotitanate of potash and sodium in an ill-closed and sufficiently heated crucible, the metallic titanium contains small reddish spangles which are easily recognized as nitruret of titanium.

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Pure titanium, first obtained by Berzelius, is a dark gray powder, resembling iron reduced by hydrogen. In this state it burns with incandescence when heated in contact with the air; muriatic acid dissolves it readily with an abundant evolution of hydrogen, and the limpid solution gives a black precipitate of hydrated protoxide. Titanium can only be obtained in a pure state by placing in a tube some trays containing sodium and fluotitanate of potash and heating them in a current of dry hydrogen, thoroughly freed from air, until the reaction is completed. After cooling, the mass is treated with boiling water.

In the authors' first experiment they operated upon an intimate mixture of 51 grms. of titanic acid and 9 grms. of charcoal in the proportions necessary to form with nitrogen the crystals of the blast-furnaces ($Ti\,Cy + Ti^3\,N$). This mixture, placed in a charcoal tray, was introduced into a charcoal tube, well protected against the action of the fire and air; the apparatus was brought to the temperature of the fusion of platinum, and a current of pure dry nitrogen, obtained from nitrate of ammonia, traversed it.

At the moment when the heat becomes sufficiently high, the nitrogen is absorbed by the incandescent mixture with such rapidity that the coal is illuminated and appears still whiter than the tube. For this purpose the current of nitrogen should be very rapid. The nitrogen suddenly disappears whatever be the rapidity, and the carbonic oxide gas produced by the reduction of the titanic acid burns with facility on escaping from the charcoal tube; thus indicating that it is not mixed with nitrogen, as a small quantity of incombustible gas prevents carbonic oxide from burning.

Thus, in this experiment, nitrogen is absorbed by the mixture with evolution of heat and light; it is the first phænomenon of this kind, a new example of a special affinity of nitrogen and titanium, manifested at a temperature which is resisted by scarcely any other known nitrogenous matter. After the operation, which should conclude with a current of nitrogen, the tray contains a metallic matter of a copper red, or a brassy yellow colour, with intermediate shades, sprinkled with brilliant crystalline laminæ, in which the presence of nitrogen and carbon is easily demonstrated: these bodies must necessarily remain there in consequence of the proportions of the mixture employed. By treating the mass taken from the tray with fused hydrate of potash, a quantity of ammonia may be obtained from it sufficient to saturate a large amount of muriatic acid, from which it may be extracted with chloride of platinum. When burnt in chlorine, this substance furnishes much chloride of titanium and a small quantity of a crystalline product, a compound of chloride of titanium and chloride of cyanogen, which is especially recognizable by the sharp odour exhaled by the crystals when in contact with water, and their irritating action upon the eyes.

When the nitrocarburetted matter, extracted from the cinder, is transferred into a charcoal crucible surrounded by a crucible of lime, heated for a quarter of an hour to the fusing-point of rhodium, it is found to be considerably diminished in volume and covered with

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octahedral crystals grouped in the form of troughs, which are only seen on the outside of the contracted but not fused mass. At the same time the flame becomes illuminated in the interior of the furnace by the presence of the titanium which it contains, and which it deposits upon cold bodies in the form of titanic acid. The crystals have thus the appearance of a matter formed by volatilization, so as to confirm the observation of Zinckey, from which it appears that the cubic crystals of the blast-furnaces must be formed by volatilization.

To prove the permeability of the charcoal vessels by the nitrogen of the air of the furnace, 25·5 grs. of titanic acid and 4·5 grs. of charcoal were placed in a closed charcoal crucible, and kept for 3 hours in a blast-furnace at the temperature of fusion of nickel. The product was slightly agglomerated, but not fused mass, of a brown colour, which under the microscope presented the metallic state of bronze. About a gramme fused with potash, evolved sufficient ammonia to permit the preparation of sublimed sal-ammoniac and the double chloride of platinum. The matter, when heated in chlorine, takes fire, furnishes liquid chloride of titanium and evident traces of crystals of chlorocyanide of titanium; after the operation there still remains a little unattacked titanic acid.

The third experiment of the authors confirms the preceding results. Sodium and fluotitanate of potash are placed in porcelain trays and heated in a glass or porcelain tube, traversed by a current of nitrogen; when the reaction is terminated, the apparatus is allowed to cool in a weak current of gas. The salt is converted into a mass of a bronze colour, which does not sensibly dissolve in boiling muriatic acid, although the evolution of a little hydrogen indicates the existence of some pure titanium. The residue is a deep brown powder, which appears metallic in the light of the sun, and is resolved by the microscope into tabular and prismatic crystals of a brassy yellow; when fused with potash this body evolves large quantities of ammonia.

When aluminium is heated in a tray placed in a porcelain tube in the midst of a current of hydrogen charged with vapours of chloride of titanium, violet chloride of titanium and chloride of aluminium are obtained, and the aluminium is converted into a brown, spongy mass which dissolves in great part in muriatic acid with evolution of hydrogen. The residue is a yellow metallic powder, which evolves ammonia when fused with potash. This is a fresh proof of the extreme affinity of nitrogen for titanium, for the formation of the nitruret of titanium in this case can only be attributed to the small quantity of air which remained in the apparatus, or which was drawn in at the same time with the hydrogen. A little yellow nitruret of titanium is also obtained, when titanium is prepared by means of fluotitanate of potash and aluminium, to which a mixture of chlorides of sodium and potassium is added as a flux. A gray metallic mass is obtained, in which the red crystalline spangles of nitruret of titanium may be detected even with the naked eye. These remain after the action of muriatic acid, and evolve ammonia with potash.

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The authors' last experiment gives an idea of the relative affinities of oxygen and nitrogen for titanium. Titanic acid heated to a bright red heat in a current of hydrogen and nitrogen, furnishes no trace of nitruret of titanium. Under these circumstances hydrogen cannot reduce titanic acid in presence of nitrogen; it requires a still more energetic agent, namely carbon.—*Comptes Rendus*, October 5, 1857, p. 480.

On some Double Æthers and Compound Æthers of Cetylic Alcohol. *By* G. Becker.

Æthylo-cetylic Æther, $\left.\begin{matrix} C^{32}\ H^{33} \\ C^{4}\ H^{5} \end{matrix}\right\} O^{2}$.—Alcoholate of sodium is dissolved in alcohol, boiled with iodide of cetyle until no further separation of iodide of sodium takes place, purified by distillation and washing with water, and recrystallized from alcohol. Readily soluble in alcohol and æther; fuses at 68° F.

Amylo-cetylic Æther, $\left.\begin{matrix} C^{32}\ H^{33} \\ C^{10}\ H^{11} \end{matrix}\right\} O^{2}$.—Prepared from amylate of sodium as in the preceding case. Resembles æthylo-cetylic æther; fuses at 86° F.

Acetic Cetylic Æther, $\left.\begin{matrix} C^{4}\ H^{5}\ O^{2} \\ C^{32}\ H^{33} \end{matrix}\right\} O^{2}$.—Obtained by treating cetylic alcohol with acetic acid and muriatic or sulphuric acid, precipitating with water, dissolving in æther, and evaporating. Oleaginous at first, but soon solidifies into a mass of acicular crystals; fuses at 64°·4 F.

Benzoic Cetylic Æther, $\left.\begin{matrix} C^{4}\ H^{5}\ O^{2} \\ C^{32}\ H^{33} \end{matrix}\right\} O^{2}$.—Obtained by heating equivalent quantities of chlorobenzoyle and cetylic alcohol, dissolving in æther and precipitating by alcohol. Forms crystalline scales, readily soluble in æther, with difficulty in alcohol; fuses at 86° F.—Liebig's *Annalen*, cii. p. 219.

ANALYTICAL CHEMISTRY.

Note on the Determination of Manganese, Nickel, Cobalt, and Zinc. *By* A. Terreil.

Manganese, nickel, cobalt, and zinc are not precipitated by sulphuretted hydrogen from acid liquids, but hydrosulphate of ammonia precipitates them completely in the form of sulphurets. The latter are insoluble in an excess of the hydrosulphate, and by means of this property the four metals above-mentioned may almost always be separated from the alkaline and earthy bases, provided the liquids acted upon do not contain ammoniacal salts or free ammonia; in the opposite case the reaction is greatly modified.

Salts of manganese, when pure, give with hydrosulphate of ammonia a precipitate of a salmon-colour, insoluble in an excess of the

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reagent. When the salts of manganese are mixed with ammoniacal salts the precipitate is dirty white, tending to light yellow; the dingy white colour of the precipitate is the more distinct in proportion as the liquid contains more of the ammoniacal salt. When the liquid contains free ammonia, besides ammoniacal salts, the precipitate is sulphur-yellow. All these different precipitates become brown by exposure to the air. But the manganese is not completely precipitated by hydrosulphate of ammonia when ammoniacal salts or free ammonia are present. The filtered liquids, which are no longer precipitated by the hydrosulphate, when evaporated and calcined, leave a residue of manganese which is more considerable in proportion as the amount of ammoniacal salts and ammonia is greater, and the hydrosulphate is more sulphuretted. Lastly, when a sufficient quantity of an ammoniacal salt is added to a salt of manganese to prevent an excess of ammonia from producing turbidity in the fluid, the manganese is no longer precipitated by hydrosulphate of ammonia. It is necessary to add to the salt of manganese, sixty times its weight of ammoniacal salt and an excess of ammonia, in order that this reaction may be very distinct.

Neutral or acid salts of nickel give a black precipitate with hydrosulphate of ammonia; the sulphuret produced is slightly soluble in an excess of the reagent. If two or three drops of hydrosulphate of ammonia be poured into a salt of nickel, to which a sufficient quantity of ammonia has been added to redissolve the oxide formed, a brown precipitate is produced, and this redissolves immediately, changing the blue colour of the liquid to a mahogany brown; if the addition of the hydrosulphate be continued, the precipitate of brown sulphuret reappears; and finally this sulphuret redissolves in great part in an excess of the reagent.

The neutral or acid salts of cobalt or zinc are completely precipitated by hydrosulphate of ammonia; but in the presence of ammonia and ammoniacal salts this reagent retains larger or smaller quantities of these metals in solution. With cobalt, the filtered liquids have a mahogany-brown colour. The cobalt and zinc retained in solution are recovered by the evaporation and calcination of the ammoniacal salts.

The oxide of chrome which dissolves in ammonia when a violet salt of chrome is treated with an excess of ammonia in the cold, is not precipitated by hydrosulphate of ammonia.

The metals above mentioned are all such of which the oxides are soluble in ammonia, and the acid solutions are not precipitated by sulphuretted hydrogen. The protosalts of iron alone did not present the characters of the metals referred to; nevertheless hydrated protoxide of iron is soluble in ammonia, and its acid solution is not precipitated by sulphuretted hydrogen. The author has ascertained that the metals of which the oxides are soluble in ammonia, but of which the acid solutions are precipitable by sulphuretted hydrogen, such as cadmium, copper, silver, &c., do not present the same characters as manganese, nickel, cobalt, and zinc, when placed in the same circumstances.

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When a liquid is freed from the metals which are precipitable by sulphuretted hydrogen, and the manganese, nickel, cobalt, and zinc are to be separated from the alkaline or earthy bases which it may contain, these metals are thrown down in the form of sulphurets by hydrosulphate of ammonia, as it is generally admitted that these sulphurets are insoluble in an excess of the hydrosulphate; but very often this is not done until after the separation of the alumina, iron, and chromium by an excess of ammonia, which retains the oxides of the above four metals in solution. These oxides doubtless pass to the state of ammoniacal bases, the salts of which no longer present the characters of those of the original oxides, as has been proved by Fremy in his memoir on the ammonio-cobaltic salts*; under these circumstances the metals of these oxides can no longer be exactly determined in the form of sulphurets.

The author has shown above, that in such cases the metals can at the utmost only be partially thrown down by hydrosulphate of ammonia. To obtain all the metal from a sulphuretted ammoniacal liquid, the latter may be boiled until it is certainly decolorized, when a precipitate is formed consisting of the metallic sulphuret mixed with sulphur; but it is still better to evaporate the liquid to dryness and calcine the product, in order to drive off the excess of sulphur and the ammoniacal salts; the metallic sulphurets are then obtained as the residue.—*Comptes Rendus*, October 26, 1857, p. 652.

New Method of determining the Silver in Argentiferous Galena. By C. Mène.

This method is founded on the solubility of oxide of silver and the insolubility of the salts of lead in caustic ammonia in excess. The author takes 20 grms. of the specimen to be analysed, pulverizes them, places them in a porcelain capsule, and boils them with nitric acid diluted with three or four times its volume of water. In a little while all the sulphur is separated and the lead dissolved. The filtered liquid is precipitated by a great excess of ammonia, and then filtered again rapidly, at the same time with an ammoniacal water. By this reagent all the oxides are precipitated at first, and afterwards those which are soluble are again dissolved; but these cause no trouble, for this liquid is treated with an excess of muriatic acid, mixed with a few drops of nitric acid to facilitate the complete precipitation of the chloride of silver. The latter may be easily separated and weighed, as all the other chlorides formed are soluble.

By this method the author determined the amount of silver contained in the following ores, &c.:—

Galena from Conflens (Ariége)	.....	silver	0·0013
„ „ Seix (Ariége)	.....	„	0·0008
„ „ Massat (Ariége)	.....	„	0·0005
„ „ Vialard (Gard)	.....	„	0·0030
„ „ Baden (Germany)	.....	„	0·0016

* See Chem. Gaz., vol. xi. p. 201.

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Yellowish litharge from Poulaouen (Finistère)	silver	0·0004
Reddish „ „ „ „	„	0·0002
Yellowish „ „ Pontgibaud (Puy-de-Dôme)	„	0·0003
„ „ „ Germany	„	0·0007
Commercial lead (gas-pipes)	„	0·0004
„ „ (unknown origin)	„	0·0006
Lead glaze for earthenware, procured at Marseilles	„	0·0012
„ (origin unknown).....	„	0·0009

This process is applicable in every case of analysis, whatever be the elements contained in the specimen under examination. Suppose a galena formed of sulphurets of lead, silver, arsenic, and antimony, of zinc, copper, and iron, with a gangue of sulphate of baryta, quartz, and clay. By ebullition in nitric acid all the sulphurets are decomposed; the sulphur separates, either in a free state or oxidized; the metals are dissolved or remain as oxides, whilst the gangues are not attacked (except the alumina of the clay, which is partially dissolved). By filtering the liquid and precipitating it by ammonia, a general magma of all the dissolved oxides is obtained; but the excess of ammonia takes up the oxide of silver, a little arsenic or arsenious acid, and the oxides of zinc and copper. After filtration the liquid is saturated with muriatic acid to convert these metals into soluble chlorides. Only the silver forms an insoluble chloride, which is precipitated.—*Comptes Rendus*, October 5, 1857, p. 484.

On a simple Reaction for the Detection of Tyrosine, Leucine, Hypoxanthine, Uric Acid, and a New Body from the Liver (Xanthoglobuline). By Professor Scherer.

Hypoxanthine, when evaporated with nitric acid upon platinum-foil, leaves a yellow, not vesicular, and but slightly lustrous residue. With caustic potash or soda in the cold, this acquires a weak reddish colour. But if the solution of this body in potash be carefully evaporated upon platinum-foil, a deeper red colour is immediately observed, passing at the margins of the fluid to a fine violet-red, which does not entirely disappear even during slow evaporation to dryness. The residue, moistened with a little water and again gently heated, becomes reddish-yellow, but the beautiful violet-red colour does not again make its appearance distinctly.

Uric acid, treated in the same way, furnishes a residue of an intensely red colour by simple evaporation with nitric acid; this becomes intensely violet-blue with solution of potash or soda, and of a beautiful purple-violet colour with ammonia.

If uric acid and hypoxanthine be present together, sometimes one and sometimes the other colour will predominate on evaporation with nitric acid and subsequent addition of the alkali, according to the relative quantities of the two substances.

The same reaction may also be applied with advantage to the detection of the smallest quantities of separated tyrosine and leucine, and also to that of another body found by the author in the liver, to which he gives the name of xanthoglobuline.

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Thus if tyrosine be evaporated with nitric acid upon platinum-foil, the first action of the hot nitric acid of about 1·200 spec. grav. causes the tyrosine, which dissolves rapidly, to acquire a bright orange-yellow colour. When evaporated to dryness it leaves a shining, transparent, deep yellow residue, and if a few drops of solution of soda be put upon this, the fluid immediately becomes deep reddish-yellow. If it be then carefully evaporated, the fluid becomes intensely blackish-brown.

This reaction is extremely easy to be established, and never fails with a little care; the author therefore prefers it to Piria's reaction, in which concentrated sulphuric acid acts for a long time upon tyrosine, after which it must be neutralized with chalk, filtered and treated with neutral perchloride of iron; for it not unfrequently happens, especially with beginners, that this reaction does not succeed.

The body above mentioned, to which the author has given the name of xanthoglobuline, and of which he has unfortunately hitherto been unable to procure a sufficient quantity to allow him to make its elementary analysis, was found originally only in diseased livers, especially in jaundice. Very recently, however, it was discovered, together with uric acid and some hypoxanthine, in the liver of the ox by Dr. Fox, who is occupied with the investigation of the latter in the author's laboratory. In its properties, and especially in its degree of solubility, it approaches most closely to tyrosine. It is usually seen under the microscope in the form of globules of a bright yellow colour. Several of these yellow globules are often agglutinated together. Like tyrosine it dissolves but sparingly in cold water, but is easily soluble in ammonia. When tyrosine is present with it in this solution, the two bodies crystallize mixed together, but the xanthoglobuline is always distinguished from the tyrosine by its strong yellow colour and distinctly globular form. As, however, tyrosine also frequently crystallizes from ammonia in globules consisting of a number of fine radiating needles, it is often difficult to distinguish the one from the other. In this case the following properties furnish data for the distinction of xanthoglobuline from tyrosine:—The globules of tyrosine are ragged all over the surface, the small pointed crystals projecting beyond the margin of the globule. If a globule of tyrosine of this kind be crushed under the covering glass, it breaks up into fragments consisting of extremely fine white needles, as indeed tyrosine crystallized from ammonia usually appears pure white, even under the microscope. The globules of xanthoglobuline, on the contrary, are always yellow, either under the microscope or with the naked eye. If a globule of xanthoglobuline crystallized from ammonia be crushed, it does not consist of needles, but of broad, yellow, laminar crystals. Xanthoglobuline never crystallizes in the fine delicate double tufts which are characteristic of tyrosine. Lastly, if cold dilute muriatic acid be poured over a mixture of tyrosine and xanthoglobuline crystallized from ammonia, the tyrosine dissolves rapidly and completely in the fluid, whilst the yellow globules of xanthoglobuline

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remain for the most part undissolved. By washing with water it may be purified, and then again crystallized from caustic ammonia.

Xanthoglobuline repeatedly crystallized from ammonia dissolves in nitric acid when heated, giving a strong yellow colour to the fluid, and when evaporated this leaves a strongly yellow, not lustrous, somewhat vesicular residue. When poured over with solution of soda, this becomes red like tyrosine. But whilst this solution of tyrosine becomes immediately deep brown, or nearly black when heated, xanthoglobuline becomes intensely purple-violet, and not, like hypoxanthine, merely at the edges of the fluid, but through the whole mass. If this splendidly coloured fluid be carefully evaporated to dryness upon platinum-foil, the colour disappears again very rapidly, and a white residue is left. If a few drops of water be poured over this residue, it dissolves without colour, whilst that obtained in the same way from hypoxanthine again becomes reddish-yellow, and that from tyrosine brownish.

This behaviour, the difference of form, and its difficulty of solution in dilute muriatic acid, clearly distinguish xanthoglobuline from tyrosine. It certainly resembles hypoxanthine in the above described reactions with nitric acid and soda, but is distinguished essentially from that substance by its being always obtained in distinct crystalline forms, whilst hypoxanthine never forms anything but an extremely fine, crystalline powder, consisting of such minute granules that they even partially pass through the filter.

Leucine also may be recognized by the same reaction as uric acid, tyrosine, and xanthoglobuline.

Thus if leucine be carefully evaporated with nitric acid upon platinum-foil, the residue is colourless and scarcely visible, if the substance be pure and free from colouring matter. If a few drops of solution of soda be poured upon this residue and heated, the leucine thus treated dissolves, according to its purity to form a limpid, yellowish or brownish fluid. If this be now carefully concentrated upon platinum-foil over the free flame of the spirit-lamp, it soon contracts into an oleaginous drop, which does not moisten the platinum-foil, but rolls about upon it without adhesion. This phænomenon is so characteristic, that, even when the leucine is not pure, but mixed with other bodies, it still constantly and certainly occurs.

As the albuminous bodies also give a reaction of the same kind as hypoxanthine and xanthoglobuline, there are still a few words to say upon this subject, and the more especially as in the investigation of organs, besides the albumen which is coagulable by heat, a considerable quantity, which cannot be coagulated by boiling, occurs dissolved in the extracted fluids. This is then usually thrown down by the addition of alcohol, when it may easily be distinguished under the microscope from xanthoglobuline which crystallizes in large globules, but not without difficulty from hypoxanthine. If a precipitate of this kind, consisting of modified albumen, or a fluid containing the latter, be evaporated on platinum-foil with nitric acid, the mass froths very strongly with a brisk evolution of gas, dissolves,

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in case it was a precipitate, only very slowly when heated, and leaves a strongly vesicular residue, which burns very easily during evaporation to dryness. If the mass, which is bright yellow when the evaporation has been carefully executed, be treated with solution of soda, it immediately becomes red, and if the mixture obtained be slowly evaporated, decolorization, or at all events a considerable diminution of the brightness of the colour gradually occurs, and in this case also a coarsely vesicular residue is left.—*Verhandl. der Würzburg. phys.-med. Gesellsch.*, and *Journal für Prakt. Chemie*, lxx. p. 406.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On Artificial Ultramarine. By Dr. H. Wilkens.

The author has published some valuable notices on ultramarine. He discusses the researches of Stölzel* on this subject, and says that they give no better explanation of the composition of the colour than any preceding treatise; for in the analysis samples of ultramarine were taken as they were furnished by the maunfactory, and their constituents determined, no care being taken as to how carefully the preparation had been washed, or as to whether it had been more or less completely desulphurized. But even attention to both these cases does not ensure pure ultramarine; for sand and clay and their impurities are taken up by ultramarine in the most varied proportions; so much so, that the product of one manufactory is different from that of others. And even in the same manufactory there may be slight variations in the composition of ultramarine, for the individual layers of clay have not exactly the same composition.

The oxide of iron found in ultramarine arises from the clay used, and is without influence on the formation of the blue colour. Ultramarine prepared in porcelain crucibles from materials free from iron, is exactly the same as that containing iron. And as much as 5 per cent. of oxide of iron added to the mass in the form of soluble salt has also no influence on the colour. In seeking the actual constituents of ultramarine, the iron, lime, potash, magnesia, sulphuric acid, and chlorine may be left out of consideration as being non-essential.

By treating ultramarine with hydrochloric acid, one part dissolves up, while another remains undissolved. In the solution alumina and soda are found in constant relation, while the amount of insoluble residue varies with each sort. At the same time $\frac{1}{5}$th of the sulphur is given off as sulphuretted hydrogen, and $\frac{4}{5}$ths is separated as sulphur. Of the following analyses, I. to V., were of ultramarines

* Chem. Gazette, vol. xiv. p. 91.

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from Wilkens's manufactory, and VI. to IX. of samples from other sources.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
SiO^3	36·74	31·14	36·15	36·31	35·77	31·89	35·73	34·27	31·68
Al^2O^3	23·97	20·80	23·25	24·81	23·75	20·59	24·95	23·68	21·03
S	12·08	10·59	11·93	11·46	12·77	9·05	12·84	10·61	10·63
NaO	18·15	17·04	18·61	20·27	19·53	17·57	19·23	18·73	18·29
FeO^3	1·49	1·32	1·50	1·03	2·28	1·80	2·52	3·00	1·62
Fe^2O^3	1·07	1·26	0·75	0·91	0·90	3·21	0·69	0·70	0·68
CaO	1·17	9·73	0·39	0·50	0·37	0·30	0·77	0·35	0·23
Residue	4·73	17·57	6·13	3·82	2·84	15·23	3·83	8·91	14·56
	99·40	100·45	98·71	99·11	98·21	99·64	100·56	100·25	98·72

If the silica, alumina, sulphur, and soda are calculated for 100, we have—

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
SiO^3	40·25	39·39	40·19	39·10	38·95	40·31	38·52	39·24	38·81
Al^2O^3	26·62	26·40	25·85	26·72	25·87	26·03	26·90	27·12	25·76
S	13·42	12·69	13·27	12·35	13·91	11·45	13·85	12·15	13·02
NaO	19·89	21·52	20·69	21·83	21·27	22·21	20·73	21·45	22·41

Wilkens gives to pure blue ultramarine the formula

$$2(Al^2O^3, SiO^3) + Al^2O^3, 3SiO^3 + NaO, S^2O^2 + 3NaS,$$

which would require

SiO^3	38·75
Al^2O^3	26·37
S	13·68
NaO	21·20

Wilkens considers that the blue colouring principle in ultramarine consists of hyposulphite of soda and sulphide of sodium. By treating ultramarine with hydrochloric acid, the hyposulphurous acid is decomposed into sulphur and sulphurous acid, and the latter acting on a portion of the sulphuretted hydrogen arising from the sulphide of sodium, sets more sulphur free.

$$NaO, S^2O^2 + 3NaS + 4ClH = 4NaCl + S + SO^2 + 3HS + HO$$
$$= 4NaCl + 4S + HS + 3HO.$$

In preparing ultramarine from clay, sulphate of soda, and charcoal, a slight access of air is necessary for the production of the blue colour; according to Wilkens's view, this access of air causes a partial transformation of sulphide of sodium into hyposulphite. When greater access of air is permitted, another portion of the sulphide of sodium which is necessary for the constitution of blue ultramarine is oxidized, and hence its colour and composition are altered. When sulphur is added to the ultramarine before ignition, it can be heated with complete access of air, for the burning sulphur unites as sulphurous acid with the excess of sulphur to form hypo-

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sulphurous acid, and preserves the sulphide of sodium from further decomposition.

Breunlin was of opinion that the sulphur in both green and blue ultramarine was in the form of polysulphide of sodium, and not in that of hyposulphite of soda, for the latter salt decomposes into sulphur and a sulphate at the temperature at which ultramarine is formed. To this Wilkens answers, that green ultramarine mixed with sulphur only requires a temperature a few degrees above the boiling-point of water to pass into blue. At this temperature hyposulphurous acid is formed, and not decomposed.

When ignited with saltpetre blue ultramarine first becomes green, which Wilkens explains by the assumption that the hyposulphite of soda is sooner oxidized than sulphide of sodium, which latter is the colouring principle of green ultramarine. Charcoal effects the same transformation of blue with green ultramarine at a red heat; in this case the hyposulphite is reduced to sulphide. When green ultramarine is heated in the air, it passes into blue even without the addition of sulphur. Breunlin thought that in this case a part of the silica of the silicate abstracted sodium from the bisulphide of sodium which became converted into pentasulphide of sodium. Wilkens remarks on this, that the change takes place at so low a temperature that silica could not be set free, and hence an action on the sulphide of sodium could scarcely take place. If pentasulphide were the condition of the formation of blue colour, green ultramarine would be converted into blue without access of air, which is however not the case. Hence the oxygen of the atmosphere plays an important and active part in the formation of the blue colour.—Liebig's *Annalen*, xcix. p. 21.

Metallic Alloy for the Formation of Medals, small Figures, &c.
By M. von Bibra.

Six parts of bismuth, 3 parts of tin, and 13 parts of lead are fused together first of all in a crucible or iron ladle; the mixture is poured out and fused again if it is to be employed in casting. It is almost as readily fusible as the well-known Rose's metal, but besides possessing considerable hardness, it has the particular advantage of not being brittle, because it possesses no crystalline structure upon the fracture. If the cast objects be bitten with dilute nitric acid, washed with water, and rubbed with a woollen rag, the elevated spots become bright, whilst the sunken portions are dull, and the casting acquires a dark grey appearance with an antique lustre. Without biting the colour is light grey. Some casts of medals taken with this alloy in plaster of Paris were so successful that the finest contours and the legend, which in the original was only legible with the lens, were completely reproduced. Calculated for 100 parts, this alloy consists of 27·27 bismuth, 59·09 lead, and 13·64 tin. As bismuth is expensive in comparison both with lead and tin, the quantity of lead might be increased and that of the bismuth diminished without injury to the valuable properties of the alloy. It is probable this mixture may be adapted for typographical purposes.—*Polytechn. Centralbl.*, 1857, p. 888.

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THE CHEMICAL GAZETTE.

No. CCCLXIV.—December 15, 1857.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On some Derivatives of Gallic Acid. *By* KARL NACHBAUR.

UNDER the guidance of Professor Hlasiwetz, the author has made a series of experiments in order to ascertain whether ternary radicals cannot be introduced into gallic acid.

This question was originally raised by the discovery, by Rochleder, of an acid which from its composition might be regarded as gallic acid, in which 3 equivs. of hydrogen are replaced by 3 equivs. of acetyle. The author has now prepared similar compounds with acetyle, butyryle, and benzoyle.

The process in general consists in bringing the protochlorides of these radicals in contact with gallic acid in a flask, which being united with a refrigeratory apparatus, allowed the evaporated fluid to be condensed and flow back. After the completion of the action, the excess of the chloride was driven off upon the water-bath, and the residuary mass purified by recrystallization.

Tetracetylogallic acid, $C^{30} H^{14} O^{18}$.—Half an ounce of gallic acid was put into a flask, and brought in contact with so much protochloride of acetyle that the mixture formed a thick paste; a refrigeratory apparatus was attached to the opening of the flask, which was then heated on the water-bath. Before the water had reached the boiling-point the mass began to froth, with an abundant evolution of vapours of muriatic acid and protochloride of acetyle. Gradually the mass became more fluid, and the evolution of muriatic acid ceased. It was then digested until no crystals of gallic acid were any longer recognizable in the flask, and the mass formed a homogeneous solution.

When this point was attained the flask was removed, the yellowish oleaginous fluid poured out into a capsule, and the excess of protochloride of acetyle driven off upon the water-bath. With its expulsion the mass became thicker, and soon solidified. When no odour of acetic acid could any longer be perceived, the residue was hard and crystalline. To purify it, it was dissolved in boiling water, the solution put into a dish and left to cool. Even whilst being poured from one vessel into the other, the fluid was rendered turbid by the separation of microscopic crystals, which speedily

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became converted into larger needles. In half an hour the crystallization was completed, as the substance is nearly insoluble in cold water. The crystals were separated from the clear mother-liquor by pressure between paper, and dried under the receiver of the air-pump. They form shining, colourless, friable needles, which scarcely dissolve in cold, and with difficulty in hot water. In alcohol and æther they are readily soluble.

Their cold aqueous solution, which has an acid reaction, furnishes a leather-yellow precipitate with a solution of sublimed perchloride of iron; the supernatant fluid is green. After neutralization with ammonia, an ink-reaction is obtained.

Acetate of lead gives a white precipitate. In this case the solution must be mixed with alcohol, to prevent the rapid crystallization of the substance, and the concealment of the reaction thereby. Tribasic acetate of lead also throws down a white precipitate.

Pure protosulphate of iron, free from peroxide, gives no coloration.

Solution of silver is reduced after the addition of ammonia.

Caustic alkalies give a red colour in the air. With protochloride of manganese and bichloride of mercury no precipitate is produced. By exposure to the air the crystals effloresce. They fuse at about 338° F., giving off a strong odour of acetic acid. When heated upon platinum-foil the substance is decomposed; the acetyle escapes as acetic acid, and there remains a shining coal, which is burnt with difficulty. By dry distillation no corresponding pyrogallic acid is obtained. The analysis of the substance dried in the air gave,—

C	51·83	30	180	51·87
H	4·46	15	15	4·32
O	43·71	19	152	43·81

Dried at 212° F.

C	52·93	30	180	53·25
H	4·42	14	14	4·14
O	42·65	18	144	42·61
$C^{30} H^{14} O^{18}$		338	97·47	
HO		9	2·53	2·50

The formation of the acid is explained thus:—

$$C^{30} H^{15} O^{18} = C^{14} H^6 O^{10} - 4H + 4C^4 H^3 O^2$$

Gallic acid.

$$= C^{14} \left\{ \begin{matrix} C^4 H^3 O^2)^4 \\ (H)^2 \end{matrix} \right\} O^{10}.$$

If tetracetylogallic acid be heated beyond 212° F., decomposition commences with evolution of vapours of acetic acid. In the attempts to prepare the salts of the acid with strong bases, decomposition also takes place.

The author made experiments with baryta, oxide of zinc, and ammonia. Carbonate of baryta was added to the hot solution of

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the acid until the effervescence ceased. Even when evaporated upon the water-bath the odour of acetic acid was perceived, and there remained a gum-like mass, which cracked when dried, and appeared to be essentially gallate of baryta. The author attempted to prepare the zinc salt. The result was the same; there remained an amorphous mass of impure gallate of zinc.

Ammoniacal gas was passed into a solution of the acid in very strong alcohol, until a solid compound separated, which was pressed between paper and dried under the air-pump. When exposed to the air, this compound rapidly became brownish. On analysis, it gave numbers which came very near those of gallate of ammonia.

Compound of Urea and Tetracetylogallic Acid, $C^{30}H^{14}O^{18}+C^{2}H^{4}N^{2}O^{2}$.—According to a memoir published by Hlasiwetz, a crystalline compound of gallic acid with urea is easily prepared. Induced by this circumstance, the author attempted to prepare a compound of tetracetylogallic acid with urea. An excess of urea (4 parts) was for this purpose dissolved with 1 part of gallic acid by the assistance of heat. On cooling, colourless acicular crystals separated, which when heated with caustic lime gave off ammonia. These crystals are more readily soluble in water than the acid alone. When agitated with ammonia and air, the solution becomes reddish, and afterwards brown. Dilute sulphuric acid decomposes the compound, with separation of crystals of tetracetylogallic acid. The following numbers were obtained by analysis:—

C	48·24	48·05
H	4·52	4·81
N	7·03	7·27
O	40·21	

Triacetylogallic Acid, $C^{26}H^{12}O^{16}=C^{14}(C^{4}H^{3}O^{2})^{3}H^{3}O^{10}$.—This compound was obtained on one occasion when an insufficient quantity of protochloride of acetyle had been employed. In this case, when after the reaction, which otherwise proceeds exactly as above described, crystals of gallic acid are still seen suspended in the thickish fluid, the mass long remains soft and tenacious after being heated on the water-bath. It is only after standing for days that it becomes crumbly and friable. If it be dissolved in water, it is particularly found to be much more soluble.

The crystals formed in the fluid are granular, their amount is smaller, and the mother-liquor still contains a considerable quantity of a substance crystallizing in fine prisms, which is essentially an impure gallic acid. The granular crystals were purified by recrystallization.

This acid is more readily soluble in water than the preceding; it is easily soluble in alcohol and æther. The aqueous solution gives a decided red colour to litmus. Perchloride of iron gives a dark green colour to the fluid. Protosulphate of iron produces a slightly greenish colour; protochloride of manganese and bichloride of mercury leave it unchanged. Caustic alkalies give it a red colour in the air. Solution of silver is reduced by it when boiled. Acetate

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of lead produces a white precipitate. The substance was dried at 212° F., and analysed.

C	52·72	26	52·76
H	4·25	12	4·05
O	...	16	43·25

If an aqueous solution of the substance be mixed with a solution of acetate of lead, a flocculent precipitate is thrown down in rather small quantity. If this be separated by filtration, a precipitate, which gradually increases, is soon formed; this is pulverulent, and has a yellowish tinge.

The amount of oxide of lead in this compound was 43·32 and 43·30 per cent., which approaches pretty closely to a compound represented by $C^{26} H^{12} O^{16} + 2PbO$.

This requires 42·96 per cent. of oxide of lead.

A compound of this body with urea could not be obtained of sufficient purity. It only crystallizes when the solution is very concentrated, and is then always penetrated by crystals of urea, which from the great solubility of the compound itself, cannot be entirely separated.

Dibutyrylogallic Acid, $C^{30} H^{18} O^{14} = C^{14} (C^8 H^7 O^2)^2 \atop (H)^4 O^{10}$. — The action of protochloride of butyryle upon gallic acid takes place with the same phænomena as that of protochloride of acetyle. When the excess of the protochloride is driven off, the whole mass does not solidify so uniformly as in the preceding compounds, but first of all a film forms upon the surface, from which the body then gradually becomes solid. After cooling, it forms a hard crystalline cake. When boiled with water, a very small portion is dissolved; the greater part remains fused at the bottom of the vessel.

The recrystallization succeeds better when the mass is dissolved in alcohol, and then so much water is added to the fluid as will just render it turbid. On cooling, fine prismatic crystals are formed; these are perfectly colourless, and have a faint odour of butyric acid. From strong alcohol, in which the mass is very soluble, it crystallizes in more solid prisms, united in druses. The crystals were dried under the air-pump; they fuse on the water-bath.

The alcoholic solution has an acid reaction. With perchloride of iron it gives an intense green colour. Alcoholic solution of acetate of lead renders it slightly turbid. Protosulphate of iron produces no change. With caustic alkalies the solution becomes red in the air. Solution of silver furnishes a white precipitate after the addition of ammonia, which is quickly reduced. Analysis:—

C	58·13	30	58·06
H	6·01	18	5·80
O	35·86	14	36·13

Benzoylogallic Acid.—The residue of the action of protochloride of benzoyle upon gallic acid is a tenacious mass when warm, and ong retains the last portions of chlorine. It is perfectly insoluble

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in water, but dissolves in alcohol in almost all proportions, and is thrown down from these solutions in a milky form by water. These conditions of solubility render its purification so difficult, that the following statements with regard to its composition are only approximate.

When the alcoholic solution evaporates spontaneously in the air, warty deposits are formed when the fluid is tolerably concentrated; these are freed from the thick sticky mother-liquor by pressure between linen. It is, however, very long before the last traces of alcohol are removed from the mass; and at about 122° F., small needles of benzoic acid may be detected in the vesicular spaces which are formed in the thickest mass. At 212° F. an efflorescence of benzoic acid sometimes forms upon the mass. Compounds of constant constitution could not be obtained. With perchloride of iron an intense green colour is produced. The alcoholic solution gives the following reactions. Alcoholic solution of acetate of lead throws down a caseous, white precipitate. Caustic alkalies give the solution a red colour when exposed to the air. Sulphuric acid, when heated, dissolves the substance with a reddish colour. On dilution with water, crystals of benzoic acid are deposited. Analyses of substances prepared at two different times with the greatest possible precautions against decomposition by heat, gave—

C	65·32	64·69
H	5·06	4·50

Calculation requires for

$C^{14}\left(\begin{matrix}C^{14}H^{5}O^{2}\\H^{5}\end{matrix}\right)O^{10}$ 61·31 carbon, 3·64 hydrogen.

for $C^{14}\left(\begin{matrix}C^{14}H^{5}O^{2}\\H^{4}\end{matrix}\right)^{2}O^{10}$ 66·66 „ 3·61 „

for $C^{14}\left(\begin{matrix}C^{14}H^{5}O^{2}\\H^{2}\end{matrix}\right)^{3}O^{10}$ 60·70 „ 3·73 „

Thus the product, containing two equivs. of benzoyle, approaches nearest to the values found.

The properties of a substituted gallic acid of this kind strongly remind one of the natural gum benzoin, and it is not impossible that this may be a similar substituted compound, which, when heated, allows the benzoyle to sublime in the form of benzoic acid, just as in the above compound. An alcoholic solution of benzoin, mixed with perchloride of iron, also gives a green colour reaction. —*Ber. der Akad. der Wiss. zu Wien*, xxiv. p. 270.

On Carajuru or Chica. *By* O. L. Erdmann.

Under this name the author has received a red dye-stuff, which agrees exactly with that described by Boussingault under the name of Chica. It is obtained from the leaves of *Bignonia Chica*, on the Orinoco and Rio Meta (*Martius*). According to Schomburgk, the Wapisianas, Tarumas, and Macusis exclusively, amongst the abori-

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gines of British Guiana, occupy themselves with the preparation of the dye Caraveru or Caravuru. The leaves of the *Bignonia Chica* are dried a little in the shade, then thrown into a trough with water, in which they begin to ferment as early as the second or third day, and during the fermentation the red colouring matter is thrown down, like indigo, in the form of a fine powder. When this process is completed, the powder is washed until all foreign matters are removed, then dried in the sun, and when half dry made up into balls, which are packed in chests of palm-wood. The Indians only use this fine colour for painting their faces, for which purpose they mix it with odoriferous resins. It has also already found its way to North America, where it is employed in dyeing cotton yellow and red, and also probably for the adulteration of cochineal.

Hancock has described a finer kind which comes from Brazil; it is sold in small packages made of palm leaves. He also states that the Indians use it for painting their bodies. For this purpose, they mix it with the oil of turtles' eggs or with araucachini balsam (from *Amyris heterophylla*, Willd.), or with the expressed oil of *Xylocarpus Casapa*. A decoction of chica is taken as a purifier of the blood.

Boussingault states that the fresh green leaves of *Bignonia Chica* give a red colour to the saliva when chewed. The tree, of which the bark is said to facilitate the separation of the colouring matter, is called by him Arayane, and he states that it is very abundant on the savannahs of Meta.

The author obtained the carajuru in lenticular cakes of 6 to 8 inches in diameter and 3 to 4 inches in thickness. Its colour is blood-red. It is moistened by water with difficulty, but when, after a considerable time, it is penetrated by water, it sinks to the bottom. If the substance be long exposed to the light, its colour passes to brownish-red, and finally to cinnamon-brown. When pressed and rubbed with a hard body, it acquires a golden green and not a coppery lustre. In consequence of a certain degree of toughness in their texture, the fragments are broken up and pounded with difficulty. Under the microscope, the mass swells up in water, exhibits numerous vegetable cells, but no trace of crystalline or other regular structure. It is perfectly insoluble in water.

Alcohol, even when boiling, only dissolves a small quantity of it, giving a red colour; the solution, when concentrated by continued boiling and evaporation, deposits a little red powder, which gradually disappears again when the fluid is long exposed to the light; the solution also bleaches in the light, and becomes brownish-yellow. If the red solution be evaporated, the dissolved matter is left as an uncrystallizable red mass.

Æther dissolves only a small quantity of the substance, and thereby acquires a yellow colour.

Chlorine immediately decolorizes carajuru, and changes its red colour into pale brownish.

Aqueous muriatic acid gives a dark brownish-yellow solution, and leaves a large quantity of slightly coloured organic matter.

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Dilute sulphuric acid, especially when assisted by heat, gives a yellow or orange-coloured solution, from which a yellowish-red, granular, but not crystalline mass is deposited on cooling. With ammonia, the solution gives a dark purple-red precipitate, which leaves a large quantity of ash when burnt.

A mixture of muriatic acid and alcohol extracts the colouring matter of carajuru with a reddish-yellow colour. Carbonate of ammonia added to the solution, produces a dark red precipitate, which, when burnt, gives a great quantity of ash.

Carbonate of soda and carbonate of ammonia, even when boiling, only extract traces with a yellowish colour; the residue becomes darker, with more of a violet tint.

Solution of caustic potash dissolves the colouring matter with a brownish-red colour. From this solution acids throw down a yellowish-red precipitate, which settles with great difficulty, and can hardly be washed, as it clogs the filter.

Ammonia extracts a portion of the colour, forming a yellowish-red fluid; the solution, when prepared by heat, becomes turbid on cooling. When mixed with acid, it becomes brownish-yellow. Ammonia or potash in alcohol dissolve the colouring matter in abundance; the colour is deep blood-red. Acids give the solution a reddish-yellow colour. Solution of potash in alcohol appears to be the most efficacious solvent of the colouring matter.

The behaviour of carajuru is very peculiar when it is treated with potash, grape-sugar and water, or alcohol in a closed flask, in the same way as in the reduction of indigo by Fritzsche's method. A violet solution is formed, which, when brought in contact with the air, immediately becomes brown. If the violet solution be allowed to run into muriatic acid without access of air, a reddish-yellow precipitate is formed, which does not settle completely even by standing for weeks; the fluid remains turbid even after filtration. The precipitate is but sparingly soluble in water with a yellow colour, and the solution becomes purple-red with carbonate of ammonia.

Stuffs could not be dyed with the red of carajuru.

By dry distillation it furnishes a thickly fluid product, which is soluble in alcohol. Its odour, when heated, resembles that of heated indigo. When burnt, it leaves a reddish-gray alkaline ash.

By treating it with nitric acid the author obtained picric acid, oxalic acid, hydrocyanic acid, and, which is worthy of notice, as a principal product, anisic acid, $C^{16} H^8 O^6$. By treating carajuru with chromic acid this was also obtained. It is produced from the red colouring matter, and this appears to be isomeric with anisic acid. This is also shown by the fact, that this red colouring matter, when treated with nitric acid, is converted into anisic acid, almost without any evolution of red fumes.

The red colouring matter of carajuru is extracted from the raw material by decoction with alcohol. The extract is evaporated to dryness, and the residue digested with æther, until the latter only acquires a pale yellow colour. The colouring matter is the portion insoluble in æther. It dissolves completely in ammonia. Muriatic

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acid precipitates it from this solution. The analysis of this colouring matter gave,—

C	59·62	63·08	63·11
H	5·34	4·95	4·93
O	35·04	31·97	31·96

These numbers closely approach those of the analysis of anisic acid, for the formula $C^{16} H^8 O^6$ requires,—

C	63·15
H	5·26
O	31·59

Journ. für Prakt. Chemie, lxxi. p. 198.

On the Formation of Glauberite and a New Double Salt of Sulphate of Soda and Sulphate of Lime. *By* J. FRITZSCHE.

During the evaporation of the solution of the residue from the preparation of muriatic acid, according to Gregory's process, the author obtained prismatic needles, which, as was shown by their analysis, consisted of a double salt, $2NaO\,SO^3 + CaO\,SO^3 + 2HO$. This double salt is also obtained, together with Glauberite, when finely-divided gypsum is heated with a concentrated solution of sulphate of soda; it then depends upon the greater or less concentration of the solution, and the temperature and duration of the heating, which compound predominates. When 50 parts of sulphate of soda is mixed with 25 parts of water, containing in suspension 1 part of sulphate of lime, prepared by precipitation and dried at the ordinary temperature, and the whole is heated and constantly stirred, the sulphate of soda alone dissolves at first, without visibly acting upon the sulphate of lime. But even at about 176° F. the fluid begins to grow thick and gelatinous, and the microscope shows the cause of this remarkable change to be the separation of a great quantity of fine acicular crystals, which make their appearance in the place of the crystals of sulphate of lime which have completely disappeared, and contain the fluid as it were sucked up like a sponge. These crystals appear to be the same double salt, $2NaO\,SO^3 + CaO\,SO^3 + 2HO$.

If the heating of the above-mentioned gelatinous fluid be continued further, other, also microscopic, crystals are observed to make their appearance between the needles, and at a boiling heat the whole quantity of the needles usually becomes converted by degrees into new crystals, which have the appearance of rhombohedra. At the same time the fluid gradually loses its gelatinous consistency; the new crystals rapidly settle to the bottom; and by pouring away the supernatant fluid, rapidly filtering the deposit, and pressing or rubbing it between bibulous paper, these crystals may be almost entirely freed from the mother-liquor. In their preparation the formation of the needles may be entirely, or at least for the most part avoided, by the employment of a larger quantity of water, for example, as much water as sulphate of soda; in such a solution no perceptible change usually takes place in the finely-divided sul-

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phate of lime before boiling, but at this temperature it is almost entirely converted into the above-mentioned crystals, which, however, are usually considerably smaller than those which are gradually formed from the needles.

The same results are obtained when acid solutions are employed instead of neutral ones, and even with a great excess of acid, neutral products alone are obtained. Thus, if a mixture of 1 part of commercial sulphuric acid with 2 parts of water be saturated at the ordinary temperature with sulphate of soda, a fluid is obtained which at about 176° F. converts the finely-divided sulphate of lime almost entirely into the acicular double salt; and it may even sometimes be kept for some time at the boiling-point without any change taking place in the needles. But if this fluid be diluted during the boiling, by stirring it and squirting water into it from a rose, the needles soon become entirely converted into the other crystals, and in this way one or the other compound may be obtained at pleasure. As the mother-liquor from either does not crystallize at ordinary temperatures, an acid fluid of this kind is much better adapted than a neutral one for the preparation of the product, because it allows a much more complete separation of the crystals from the mother-liquor.

The rhombohedriform crystals proved on analysis to be Glauberite; they are anhydrous, and undergo no loss of weight by ignition.

As native Glauberite belongs to the hemiprismatic system, the artificial microscopic crystals also are doubtless no rhombohedra, as they appear to be under the microscope, but shortened prisms. They are obtained of $\frac{1}{80}$th line at the utmost, but frequently of scarcely $\frac{1}{600}$dth line in diameter.

The behaviour of water to Glauberite is different according as it has or has not been calcined, and this is the same both with the artificial and with the natural Glauberite from Villarubia. The uncalcined double salt is transparent; when brought in contact with water under the microscope, it is seen to dissolve gradually, and at the same time crystals of sulphate of lime separate, just as the author has described above for the other double salt. First of all the crystals appear as if eaten into, but in a very short time crystals of sulphate of lime are produced in their vicinity, both seated upon them and also around them; these increase rapidly and become developed partly into stellate or fascicular aggregations close to the disappearing crystals of the double salt, and partly in separate individuals at some distance from them; of these, the latter especially sometimes attain a length exceeding double the diameter of the artificial crystals of Glauberite. If the quantity of water employed be insufficient for the solution of the sulphate of soda, or if many crystals lie close together, they frequently do not entirely disappear, and there remain between the crystals of sulphate of lime, rounded, but always transparent portions of the crystals; by moving the fluid, or adding more water, these also disappear rapidly and completely.

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The calcined double salt, which is essentially distinguished from the uncalcined salt even in the dry state, or when moistened with alcohol by its opacity and the rough surface of its crystals, behaves differently; the cohesion of the crystals is considerably diminished by calcination, as they may be crushed between two glass plates much more easily than before, so that a change in the state of aggregation of the crystals has been brought about by the calcination. When water is poured over the calcined crystals, they either retain their form completely or partially, or fall entirely or partially into a fine powder which only exhibits an indistinct crystalline structure. In this case, there is no doubt that the sulphate of soda alone is dissolved, whilst the sulphate of lime remains undissolved like a skeleton; of this, indeed, a small quantity is also dissolved, which is again deposited in hydrated crystals during evaporation, but it is comparatively very small in quantity, and the crystals of sulphate of lime formed are far smaller than those produced from the hydrated double salt.

This behaviour leads us to two conclusions:—in the first place, the Glauberite of Villarubia must be formed in the humid way; and secondly, the calcined Glauberite can no longer be a double salt, or, in other words, its two constituents are no longer chemically combined, but only in mechanical juxtaposition. This also applies to the double salt first described, which, after calcination, exhibits the same difference as Glauberite when treated with water.—*Bull. de St. Pétersb.* xvi. p. 124.

On Stibmethæthylium and its Compounds.
By Dr. S. Friedländer.

It was already shown by Löwig's investigations of stibæthylium, and Landolt's memoirs upon stibmethylium, that the bases of this kind must be regarded as ammonium in which the atoms of hydrogen are replaced by methyle, æthyle, &c. Merck's investigations prove this supposition to be perfectly correct. The latter prepared

$$Sb\left\{\begin{matrix}Ae^3\\H\end{matrix}\right. \text{ corresponding with the type } N\left\{\begin{matrix}H^3\\H\end{matrix}\right.$$

The author has now, at Löwig's instigation, prepared mixed compounds in which the remaining H is replaced by a radical capable of displacing metal, namely compounds of stibmethæthylium. They are as follows:—

Iodide of Stibmethæthylium, $Sb(Me\,Ae^3)I$.—This compound furnishes the material for all the following ones. Stibæthyle is first prepared by treating an alloy of antimony and potassium with iodide of æthyle*. The stibæthyle must be free from iodide of æthyle, which is effected by treating it a second time with the alloy.

The iodide of methyle, which is employed in the preparation of iodide of stibmethæthylium, need not be anhydrous.

To prepare the compound, the stibæthyle is put with water into

* See Chem. Gaz. vol. viii. p. 201.

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a bottle filled with carbonic acid, and iodide of methyle is added to it in small quantities. As soon as the mixture is heated in lukewarm water, which must not exceed in temperature the boiling-point of iodide of methyle (109° F.), the fluid becomes turbid, but this turbidity disappears again immediately on shaking it, because the iodide of stibmethæthylium, which is insoluble in stibæthyle, dissolves very readily in water. Iodide of methyle is now added until the odour of stibæthyle disappears, and the operation may then be recommenced. With care, the formation of oxide of stibæthyle may be entirely avoided.

The fluid standing over the residue of iodide of methyle, and containing the iodide of stibmethæthylium in solution, is drawn off by a pipette and slowly evaporated in the water-bath. During this process a yellow substance, such as was observed by Löwig in the preparation of iodide of stibæthylium, is never formed, but very beautiful crystals are always deposited, often attaining a size of 25 millims., and in the fresh state exhibiting a strong glassy lustre, which, however, subsequently passes into a dull nacreous lustre. They appear to be rhombic prisms. These crystals are always anhydrous, stable in the air, readily soluble in water and alcohol, and nearly insoluble in æther. The solution is perfectly transparent, and deviates the plane of polarization to the right. It is inodorous in the cold, but at 212° F. exhibits a peculiar odour, although no decomposition could be detected by analysis. It also possesses an intensely bitter taste. At 68° F., 1 part of the salt dissolves in about 2 parts of water. Analysis:—

Sb	32·98	33·50	1	120	34·38
C	23·03	23·55	14	84	24·07
H	5·57	5·38	18	18	5·16
I	36·03	35·99	1	127	36·39

Iodide of Stibmethæthylium and Mercury, $Sb(Me\,Ae^3)\,I, 3HgI$, is produced when a boiling saturated solution of iodide of stibmethæthylium is mixed with a hot solution of bichloride of mercury. A yellowish-white precipitate is formed; when further heated, this fuses into an oil, and on cooling forms a pale yellow, crystalline mass. The solution contains chloride of stibmethæthylium. Formation:—

$$4Sb(Me\,Ae^3)\,I + 3HgCl = Sb(Me\,Ae^3)\,I, 3HgI + 3Sb(Me\,Ae^3)\,Cl.$$

It is insoluble in water, and difficult of solution in alcohol and æther. It is thrown down from its alcoholic solution in the form of a yellowish powder by the addition of water. The aqueous solution when evaporated deposits it in yellow, shining crystals. Analysis:—

Stibmethæthylium ..		..	1	222	21·56
Mercury.....	28·68	28·59	3	300	29·12
Iodine.....	50·15	48·65	4	508	49·32

Iodide of Stibmethæthylium and Mercury, $Sb(Me\,Ae^3)\,I + 2HgI$, is produced by bringing the solution of iodide of stibmethæthylium

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in contact with freshly precipitated iodide of mercury, until the latter undergoes no further change of colour. It crystallizes in small rhombic tables.

Chloride of Stibmethæthylium, Sb (Me Ae^3) Cl, is produced by the contact of 3 equivs. of bichloride of mercury with 2 equivs. of iodide of stibmethæthylium, and also by treating the oxide of stibmethæthylium with muriatic acid.

Oxide of Stibmethæthylium, Sb (Me Ae^3) O.—The iodide is treated with oxide of silver, or, which is better, the sulphate of stibmethæthylium is decomposed with an exactly sufficient quantity of hydrated baryta. The solution must be evaporated under the air-pump, because the oxide attracts carbonic acid.

It is a thick, oily, somewhat yellow fluid, of an intensely bitter taste, and a strong alkaline reaction. It is insoluble in water and alcohol. It expels ammonia from its salts, and also the bases from salts of copper, iron and manganese. Alumina and oxide of zinc are dissolved by it. It is not volatile, and gives salts with all the oxyacids. The salts are all more or less soluble in water and alcohol. Some of them deliquesce in the air. The crystallizable salts often contain no water of crystallization. The author has prepared,—

Sulphate of Stibmethæthylium, Sb (Me Ae^3) O, SO^3, in white, shining, anhydrous crystals, of a strong bitter taste, deliquescent, fusing at 212° F.

Nitrate of Stibmethæthylium, Sb (Me Ae^3) O, NO^5.—Forms beautiful silky needles, readily soluble in water; they attract water from the air but slowly, and explode violently on red-hot charcoal. Anhydrous.

Carbonate of Stibmethæthylium, Sb (Me Ae^3) O, CO^2.—A white resinous mass, behaving exactly like carbonate of ammonia. It is prepared from the sulphate by treatment with carbonate of baryta.

Formiate of Stibmethæthylium, Sb (Me Ae^3) O, C^2 HO^3.—Prepared by treating formiate of lead with a hot solution of iodide of stibmethæthylium in equivalent proportions; is very difficult of solution in cold water and alcohol; boiling water dissolves a great quantity of it.

The *Acetate* and *Butyrate* are both anhydrous, and similar in composition to the preceding. They crystallize, the first in needles.

The *Neutral Oxalate*, 2Sb (Me Ae^3) O, + C^4 O^6, forms beautiful anhydrous needles of a glassy lustre.

The *Acid Salt*, Sb (Me Ae^3) O, HO, C^4 O^6, does the same; the needles are readily soluble in water. The salts are produced when the acid and base are brought in contact in proportions corresponding with the formulæ.

The *Tartrate*, Sb (Me Ae^3) O, C^8 H^4 O^{10}, does not crystallize, but forms a syrupous fluid of a bitter taste, which attracts moisture from the air.

Sulphuret of Stibmethæthylium, Sb (Me Ae^3) S.—If the solution of the oxide be saturated with sulphuretted hydrogen gas, and evaporated without access of air, the sulphuret remains in the form of

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an oily non-crystalline mass, which is readily soluble in water and alcohol, smells strongly of sulphuretted hydrogen, and behaves towards metallic salts in the same way as sulphuret of ammonium.

Cyanide of Stibmethæthylium.—If hydrocyanic acid be added to a solution of stibmethæthylium, the solution contains the cyanide in the form of a limpid fluid, smelling strongly of hydrocyanic acid, which, when treated with muriatic acid, evolves hydrocyanic acid, and behaves towards metallic salts like cyanide of potassium, but exhibits the peculiarity, that, when muriatic acid is poured over the concentrated solution, a white precipitate, insoluble in water, is formed, which is not the case if the solution be previously diluted with much water.—*Journ. für Prakt. Chemie*, lxx. p. 449.

Note on Achilleic Acid. *By* Professor H. Hlasiwetz.

Zanon's achilleic acid was recently prepared in the author's laboratory according to his process*, when the author convinced himself that it is not malic but aconitic acid. It is combined with lime in the plant.

The pure acid is not volatile, is readily soluble in water, alcohol, and æther, has a strong, purely acid taste, and saturates the alkaline bases completely.

The solutions neutralized with potash and ammonia dry into gum-like masses. If the acid still contain much of the subsidiary constituents of the nature of tannic acid, solutions rendered alkaline become yellowish-brown when exposed to the air. Lime-water is not rendered turbid by the acid when warm. The solution obtained by saturation with carbonate of lime, gave, on evaporation, a gelatinous mass, which dried with undulating elevations. Solution of sugar of lead furnishes a flocculent white precipitate which does not become crystalline.

Baryta-water produces a voluminous white precipitate. The silver precipitate from the acid partially saturated with ammonia, rapidly became black by exposure to light. The compounds with potash and soda described by Zanon might have been the subsalts. His description of their appearance and taste agrees exactly therewith.

He also obtained amorphous salts of ammonia and magnesia. On the other hand, he states that the solution of the acid is not precipitated by acetate of lead.—*Bericht der Akad. der Wiss. zu Wien*, xxiv. p. 268.

On Nitrate of Bismuth as a Test for Grape-Sugar. *By* Dr. C. Grischow.

The author has found that a urine, free from grape-sugar, blackened the basic nitrate of bismuth employed in Böttger's test. The urine examined contained an abundance of albumen.—*Archiv der Pharm.*, cxli. p. 281.

* See Chem. Gaz. vol. v. p. 32.

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Behaviour of Uric Acid to the Alkaline Solution of Oxide of Copper. *By* N. J. Berlin.

Fehling's fluid, when boiled with a little uric acid, gives at first a yellow, and finally a reddish-brown precipitate. In the cold, it furnishes a white precipitate of protourate of copper (not perurate), which is crystalline and stable in the air. This white precipitate remains unchanged when boiled with water and solution of potash; with solution of peroxide of copper and potash, it becomes brown or cinnabar-red.—*Journ. für Prakt. Chemie*, lxxi. p. 184.

On the Composition of the solid part of Olive Oil. *By* W. Heintz.

In 1855 the author opposed Collet's statement, that margaric acid occurs in olive oil. At the author's recommendation, Hetzer has made an investigation of this oil in his laboratory, and found that palmitic acid is contained in it.

Besides this acid, oleic acid and a second solid acid is contained in that portion of the oil the melting-point of which is higher than that of stearic acid.—*Journ. für Prakt. Chemie*, lxx. p. 366.

On the Formation of Isatine by Ozone. *By* O. L. Erdmann.

The author has found that pure indigo-blue, made into a paste with water, is readily converted into isatine by ozonized air.—*Journ. für Prakt. Chemie*, lxx. p. 209.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Behaviour of Zinc in the Atmosphere.
By Dr. Max Pettenkofer.

The Principal of the Bavarian Commission of Railways addressed the following question to the author,—"To what thickness should a coating of zinc be laid upon iron, in order to protect the latter metal permanently from oxidation?" As a starting-point for the solution of this question, the author required a fragment of a zinc roof, which had already been exposed as long as possible to the open air. The author obtained a zinc plate of about 1½ square feet from a roof in Munich, which had for fully 27 years been subjected to all the varying influences of the atmosphere. Both surfaces of the plate were covered with a coat of oxide; the upper surface with a thick white one, the lower with a thin gray one. The author thought that he must regard the upper one especially, as that which had been most exposed to the influences of the atmosphere. On the lower surface the oxidation was inconsiderable, and moreover for 27 years there had been no opportunity of oxide being carried away from this part, so that there was still more reason for limiting the investigation to the upper surface.

The coat of oxide on the upper surface exhibited a somewhat

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different thickness on different parts, and even here and there different colours (between whitish and yellowish). It adhered very firmly to the surface of the zinc, it being impossible to scratch it off with the nails, so as to lay bare the bright metal. The coat of oxide dissolves quickly in hot solution of potash, prepared with 1 part of hydrate of potash and 6 parts of water. If the solution of potash be more concentrated, or the temperature be raised to the boiling-point, an evolution of hydrogen gas takes place, indicating that unoxidized zinc is also dissolved in the solution of potash. When the coat of oxide has been removed in this way, a metallic surface of very crystalline appearance (*Moiré métallique*) is seen below it, an indication that the zinc is not uniformly oxidized from the surface, but in the direction of the faces of the crystals, and that it cannot consequently be a matter of indifference whether a zinc surface be an aggregate of larger or smaller crystals, because by this means the elevations and depressions in which the oxidation goes on, will become larger or smaller, and a coarsely crystalline plate will be sooner perforated by the rust than a finely crystalline one.

The yellowish colorations and streaks upon the surface of the coat of oxide, correspond with darker streaks upon the metallic surface. They appear to be due to the action either of the rollers or of some other iron.

The proximate constituents of the coat of oxide are oxide of zinc, carbonic acid and water, together with very small quantities of other metallic oxides (oxides of iron and lead); from the analysis it will be seen that it may be regarded as a hydrocarbonate of zinc. Besides these, variable quantities of street-dust are found situated in the numerous pores; this is recognizable as a mud insoluble in solution of potash.

To determine the weight of the coat of oxide upon a given surface, strips of the plate of a rectangular form were cut off, and their lower surface freed from its small quantity of oxide by the file, and somewhat polished. They were then weighed and put into a solution of 1 part of hydrate of potash in 6 parts of water, heated to 140° F. The upper coat of oxide was dissolved away in 3 or 4 minutes, when the strips were laid in distilled water, freed with a hair-pencil from the muddy portions adhering to them, washed, dried at 212° F., and weighed. The loss of weight was equal to the weight of the coat of oxide.

To ascertain the amount of zinc contained in this coat of oxide, it was precipitated from the filtered potassic solution by sulphuret of ammonium; the sulphuret of zinc, which was rendered brownish by a little sulphuret of lead, was dissolved in dilute sulphuric acid, precipitated whilst boiling with carbonate of potash, washed, ignited, and weighed as oxide of zinc.

I. A first strip of plate of 31 Bavarian decimal lines in length and 5·75 lines in breadth (=2·4025 square-tenths of an inch in surface), weighed 7·939 grms., and lost 0·2255 grm. by the treatment with potash; the potassic solution gave 0·130 grm. of oxide of zinc, representing 0·1043 grm. of zinc.

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II. A second strip from another part of the plate of 31 lines in length and 6·8 lines in breadth (=2·108 square inches in surface), weighed 7·354 grms., lost 0·221 grm., and furnished 0·101 grm. of oxide of zinc, representing 0·0811 grm. of zinc.

If we calculate from experiment I. the quantity of reguline zinc for 1 square foot of the coat of oxide, it appears to be 4·341 grms., whilst experiment II. gives a quantity of 3·847 grms. It is not quite correct to come to a conclusion as to the weight of the oxidized plate from these numbers, because the author has only taken into consideration the chemically pure zinc, whilst the commercial metal from which the plate is made, always contains some portions of foreign metals, although only in small quantities. If we reckon the impurities at 4 per cent. we get for 1 square foot,—

in experiment I..... 4·521 grms. crude metal,
„ „ II..... 4·007 „ „ „

It was only possible to investigate the further composition of this zinc-rust by a round-about-way. As the qualitative examination of the zinc-rust only gave essentially carbonic acid and water in addition to oxide of zinc, it was thought that the entire chemical composition might be ascertained if the rust adhering to a measured surface, the amount of oxide of zinc contained in which was calculated from the average of the two preceding quantitative analyses, was heated until the carbonic acid and water were expelled, and if the carbonic acid and water could be collected separately and weighed. This could be easily effected when an exactly measured piece of zinc plate, from which the lower coat of oxide had been removed, was cut into strips, put into a combustion tube, and heated to a temperature at which carbonic acid and water would separate from oxide of zinc, at the same time that a current of atmospheric air free from carbonic acid and water was drawn through the tube by means of an aspirator; this would conduct the water and carbonic acid from the zinc-rust into the apparatus used in organic analysis, when they might be absorbed and weighed. In this way 8·95 square inches of surface gave 0·200 grm. of carbonic acid and 0·169 grm. of water, from which calculation gives for 1 square foot of zinc plate, 2·2346 grms. of carbonic acid and 1·8883 grm. of water. From the preceding determinations we know that the average quantity of oxide of zinc upon the square foot may be taken at 5·1175 grms., so that we have all the elements for forming an idea of the exact composition of the rust upon our zinc roofs. Regarding the amount of carbonic acid found as 1 equiv., the quantity of water represents 2·05 equivs., and that of oxide of zinc 1·25 equiv. Expressed in direct proportions, the zinc-rust contains

5 equivs. oxide of zinc,
4 „ carbonic acid,
8 „ water,

in chemical combination. It is remarkable that the simplest expression for the basic carbonate of zinc which is obtained by the

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precipitation of solutions of zinc salts by carbonate of potash or soda, also contains 5 equivs. of oxide of zinc, $2(ZnO.CO)^2 + 3(ZnO.HO)$. If it be desired to express the result of the author's analysis in a formula, we must probably write $4(ZnO.CO^2) + ZnO.HO + 7HO$, according to which we should have a compound of 4 equivs. of carbonate of zinc and 1 equiv. of hydrated oxide of zinc with 7 equivs. of water. We possess a very detailed investigation by H. Rose, of the numerous proportions in which oxide of zinc, carbonic acid and water combine with each other, when equal equivalents of carbonate of soda and sulphate of zinc are mixed together. The air-dried compound which is obtained by mixing cold concentrated solutions, gives

5 equivs. of oxide of zinc,
2 „ of carbonic acid,
4 „ of water,

so that the zinc-rust, with the same number of equivalents of oxide of zinc as the compound prepared in the humid way and investigated by H. Rose, contains exactly double the number of equivalents of water and carbonic acid. The author, however, does not consider the formula of the zinc-rust as established, since the formula given by him is only based upon a single specimen of a certain age.

It would be incorrect to imagine that the quantity of oxide of zinc found in the rust, represents the quantity of metal which has been oxidized by exposure to the air in a certain time. It could not but be supposed, that a great portion of the oxide was dissolved and carried away by the rain-water. To form some judgement as to the amount of this, a portion of the old zinc plate was arranged in such a way that within 45 minutes 3 kilogrms. of water might flow in a uniform stream over a surface of 123 square inches. This uniform stream was produced by some rows of strings which were put transversely and somewhat obliquely upon the upper part of the plate, the latter being supported at an angle of about 45°. By a greater or less elevation of the plate, so that the fall of the water in the direction of the strings was altered, the uniform flow of the water could be easily regulated. Distilled water was employed; it had been exposed to the open air in a shallow vessel until it produced a strong turbidity with basic acetate of lead. These 3 kilogrms. of water were allowed to flow ten times over the surface thus arranged into a porcelain cup; the water evaporated was replaced. Finally, a few drops of sulphuric acid were added, and the water was evaporated; the oxide of zinc was then separated from the residue and weighed. The 3 kilogrms. of water thus passed over the zinc contained 0·114 grm. of oxide of zinc = 0·0886 of zinc. This zinc was partly dissolved in the water and partly carried away mechanically.

The author regarded the tenfold action of 3 kilogrms. of water as equal to one action of 30 kilogrms. The average annual fall of rain in the neighbourhood of Munich is not taken too high, if we suppose it to be 2 Bavarian feet for a square foot of roof-surface inclined at an

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angle. For 123 square inches, therefore, there would be 2·46 cubic feet of water. A Bavarian cubic foot of water weighs 24861·29 grms.; 2·46 cubic feet consequently represent 61 kilogrms. which would have carried away 0·1801 grm. of zinc. According to this the annual loss by rain for 1 cubic foot of roof-surface would be 0·1464 grm. As in the present case this loss must have taken place 27 times, we get 3·9528 grms. as the entire loss in pure zinc by atmospheric water; and supposing, as above, that 4 per cent. of foreign metals are associated with the zinc, we get a loss of 4·1175 grms. upon 1 square foot of zinc plate in 27 years. Adding to this the average amount found for the coat of oxide of 1 square foot, the total loss of the zinc plate amounts to

a. Still present in the rust.....	4·264	grms.
b. Carried off by rain-water, &c..	4·117	„
Total....	8·381	

We may consequently assert that in the course of 27 years a zinc roof is oxidized to the extent of 8·381 grms. per square foot, of which nearly one-half is carried off by the water condensed from the atmosphere.

The question whether a coat of oxide can ever completely prevent the further progress of the oxidizing process in the subjacent metal, is consequently answered in the negative. The destruction of zinc roofs is certain and unavoidable. Nevertheless no one need hesitate in the least upon this account to make use of zinc roofs in future, for the destruction proceeds with extreme slowness, and probably becomes more gradual as the coat of oxide grows thicker. If we suppose 8·3815 grms. of zinc (its spec. grav. being taken according to Karsten at 6·2) spread over a surface of 1 square foot, the height of this layer appears to be 0·00543 line. A layer which is only five-thousandths of a line in thickness, requires, as we have seen, 27 years to be eaten entirely away, and from this we may calculate the duration of a zinc roof, composed of plate 0·25 line in thickness, as $46{\cdot}04 \times 27 = 243$ years, leaving out of consideration the oxidation of the lower surface, which never comes in contact with water, and the slackening of the oxidation by the increase of the upper coat of oxide, as being two values which may nearly compensate each other. In 243 years all the metallic zinc would be eaten away by the atmosphere. But the roof would be perforated and useless before this period, because as this metal, from its crystalline structure, is attacked in the direction of the faces of the crystals, the rust will penetrate more deeply in one place than in another. Prof. Lamont has made some microscopic observations upon the size of the elevations and depressions of the apparently crystalline surface of the zinc plate freed from oxide by treatment with solution of potash; the greatest depressions amounted to 0·028 line, or $\frac{1}{10}$th of the original thickness of the zinc.—Dingler's *Polytechn. Journal*, cxlv. p. 296.

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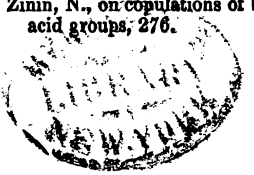

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